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The Production of Hydrogen Peroxide in Water by Alpha-Rays*

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The ultraviolet absorption spectrum of air-free water irradiated with alpha-rays has been photographed between 2200 and 2800A. The spectrum appears to belong to a dilute aqueous solution of hydrogen peroxide. The gases evolved from the irradiated water contain hydrogen in excess of an electrolytic mixture. The parallel variation of excess H_2 pressure and H_2O absorption is consistent with Duane and Scheuer's hypothesis. Apparatus has been developed in which excess H_2 and H_2O absorption can be measured simultaneously at different times without disrupting the normal course of an experiment. The method is applicable to other radio and photochemical reactions.

INTRODUCTION

MANY radio and photochemical reactions in aqueous solutions are ascribed to the primary decomposition of the water molecules and to the secondary formation of hydrogen peroxide. In 1912 Rosanoff[1] suggested that the absorption of ultraviolet rays by radioactive substances is conditioned by the emanations emitted, and by the hydrogen peroxide formed under the influence of this emanation. Other investigators at that time regarded the part played by hydrogen peroxide as insignificant.

Kernbaum[2] found that distilled water free from air when exposed in a quartz vessel to the sun's rays shows evolution of gas after a few hours. Using Shonbein's reagent, hydrogen peroxide was detected. The quantity was larger when the experiments were carried out in the presence of air. He concludes that water undergoes decomposition and that hydrogen peroxide is an intermediate compound in the reaction. Hydrogen peroxide production by radiant energy is of biological interest, for there are those who believe that ultraviolet rays exert an influence on microorganisms by virtue of the H_2O_2 they produce, and that the intense action of the direct rays is due to a production of peroxide within the organisms themselves.[3]

Clark, in his review of the biological effects of x-radiation,[4] lists the formation of hydrogen peroxide when water containing dissolved oxygen is irradiated among the biologically significant effects of x-rays. Later, in the same paper, he mentions the important conclusion of Fricke that the activated water molecule rather than the direct effect of the rays or the formation of hydrogen peroxide may be responsible for the action on living cells. The role of hydrogen peroxide in the complex organic molecular systems is extremely difficult to ascertain and its formation in the more simple systems has not been proved experimentally in many cases.

* The experimental work was done in the Laboratory of Biophysics and the Cancer Institute, Minnesota General Hospitals, Minneapolis.

[1] Rosanoff, J. Russ. Phys. Chem. Soc. **44**, 1146 (1912); J. Chem. Soc. **102**, 875 (1912).

[2] Kernbaum, Farm. Polsk. **71**, 16 (1913).

[3] T. H. B. Bedford, Brit. J. Exp. Path. **8**, 437 (1927).

[4] George L. Clark, Radiology **26**, 295 (1936).

Eight-tenths normal sulphuric acid in water added to ferrous sulphate after x-ray irradiation oxidizes the ferrous ion to the ferric ion, although in an irregular manner.[5] The reaction is ascribed to the formation of H_2O_2 in the acid. The reduction of chromate by x-rays has been found to be related also to the production of H_2O_2.[6] Fricke found that oxygen dissolved in water is reduced to H_2O_2 when irradiated with x-rays.[7] If the water is air-free then x-rays do not decompose it and H_2O_2 is not formed.[8, 9] On the other hand, air-free water is decomposed by alpha-rays as has been shown by the writer in some work not yet published. The inability of x-rays to decompose air-free water in contrast to the ability of alpha-rays to do so suggests two distinct mechanisms which hitherto have been considered similar.

The notion of H_2O_2 synthesis in aqueous solutions probably originated from the well-known investigations of Duane and Scheuer[10] in which water was irradiated with alpha-rays. Hydrogen and oxygen were liberated. The gases, however, were not present in electrolytic proportions but always contained an excess of hydrogen. The excess was less than 50 percent, and gradually decreased as the experiment proceeded. The writer has found that if the experiments continued long enough then the excess hydrogen disappeared almost entirely.[11] In a more recent work[12] the excess hydrogen from air-free water has been found to be 100 percent early in the experiments.

Duane and Scheuer concluded that hydrogen peroxide was formed by the action of nascent oxygen on water and thereby giving an excess of hydrogen in the liberated gases. They explained the decrease of excess hydrogen as occurring when the quantity of H_2O_2 reached an amount such that its rate of decomposition, both spontaneous and that caused by the rays, is equal to its rate of formation. Their hypothesis seems logical in part but no conclusive experimental evidence has been produced either to prove or disprove it. The various reported steps in the reaction are mostly speculative. Whether nascent O_2 acts on the H_2O molecules or H_2 and O_2 combine to form H_2O_2 has not been confirmed one way or the other; however, the results on air-free water indicate that if nascent oxygen is present it has originated from decomposed water and not from dissolved oxygen.

For the sake of clearness the reactions may be described by the following expressions:

$$2H_2O(+\alpha) = 2H_2 + O_2 \uparrow \rightarrow H_2O_2 + H_2 \uparrow,$$
$$H_2O_2(+\alpha) = H_2 + O_2,$$
$$H_2O_2 \rightarrow H_2 + O_2 \text{ (Thermal)}.$$

From these reactions there result two experimentally measurable end products, namely H_2O_2 and the gases O_2 and H_2 which have certain reasonable quantitative relationships. For example, each H_2O_2 molecule formed or decomposed should give rise to one more or one less excess H_2 molecule (excess of H_2 over electrolytic proportions of H_2 and O_2). Therefore, H_2O_2 concentrations calculated from measured excess H_2 gas should agree with measured concentrations. The rise and fall of H_2 pressure should also run parallel to H_2O_2 concentrations. In order to test these suggestions an experimental method has been developed in which H_2O_2 in the irradiated water and excess H_2 in the liberated gases can be measured simultaneously at many different times without disrupting the normal course of the experiments. The method gives promise of being applicable to the study of many other radiochemical reactions. Another desirable feature is that the irradiated water is made gas-free. Therefore it is possible to determine if alpha-rays and x-rays are alike in the latter's inability to decompose air-free water and to cause the formation of H_2O_2. A description of the method and of some of the first results are described. Because of the author's transfer to a limited stay in China further experiments have ceased temporarily.

Experimental Method

The water was purified in an all Pyrex vacuum still (Fig. 1) and was subjected to the rays in a

[5] Hugo Fricke and Samuel Morse, Phil. Mag. **7**, 129 (1929).
[6] Hugo Fricke and E. R. Brownscombe, J. Am. Chem. Soc. **55**, 2358 (1933).
[7] Hugo Fricke, J. Chem. Phys. **2**, 349 (1934).
[8] O. Risse, Zeits. f. physik. Chemie **A140**, 133 (1929).
[9] Hugo Fricke and E. R. Brownscombe, Phys. Rev. **44**, 240 (1933).
[10] Wm. Duane and O. Scheuer, Le radium **10**, 33 (1913).
[11] Carl E. Nurnberger, J. Phys. Chem. **38**, 47 (1934).
[12] Not yet published.

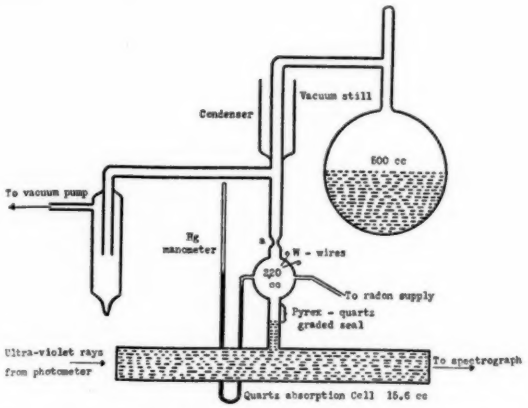

FIG. 1. Vacuum still, reaction chamber and absorption cell for the study of alpha-ray irradiation of air-free water.

quartz chamber. The usual precautionary measures common to the preparation of conductivity water were carefully observed. The reaction chamber was sealed directly to the still in order to eliminate contamination of the pure water by the air in the laboratory and by contact with the apparatus which otherwise would have been used to transfer the water from the still to the chamber.

The reaction chamber consists of two parts. At the bottom a 10 cm quartz cell serves as a reservoir for the irradiated water and as absorption cell in the spectrophotometric measure of hydrogen peroxide. Above the cell, but connected to it by means of a small tubular Pyrex to quartz graded seal is a 2.20 cc Pyrex bulb. The evolved gases collected and were analyzed in this bulb. The quantity of gas was measured at constant temperature and volume. Pressures were read on the 2 mm bore mercury manometer. The excess hydrogen was separated from the gaseous mixture by means of explosions set up by repeated sparks between tungsten wires sealed in the small bulb. The residual gas was all hydrogen.

Some difficulty was experienced by cracking of the quartz-Pyrex graded seal. Pyrex glass is known to become cracked by penetrating irradiation. Many of the Pyrex reaction chambers which the author used in earlier work had to be discarded after prolonged alpha-ray bombardment because of deep cracking, particularly around sealed in metal electrodes. Similar phenomenon has not been observed in quartz by the author, but in the quartz-Pyrex seal deep cracks appeared after much less irradiation than required to crack Pyrex alone. Most of the deeper cracks came in the Pyrex end of the seal; however, some shallow ones extended into the quartz. The cracked tube was readily fixed by heating to the softening point. Although quartz is colored by alpha-rays, the absorption characteristics of the cell itself were not altered because the water protected the surfaces from intense exposure.

After water had been distilled into the quartz cell and the tube had been sealed at *a*, radon was admitted through the capillary radon supply tube. The latter was subsequently sealed a few millimeters from the chamber. The method of releasing the radioactive gas has been described in detail elsewhere.[9] At this stage, the reaction chamber and the manometer were completely separated from the still and the radon supply. The small unit was portable and could be moved readily from the constant temperature water bath to the optical analyzing system.

A portion of the radioactive gas diffused into the water in the quartz cell. The amount of dissolved radon, and therefore that which determines the principal effective alpha-ray action, depends on the dimensions of the reaction chamber. If quantitative gas yields per unit of irradiation are desired, then these physical factors cannot be neglected without introducing considerable errors. In the experiments described here gas yields per unit of exposure are not important and so no attempt is made to calculate the effective radon. It will suffice to say that the results of previous experiments point to the conclusion that the diffusion of radon into the water was nearly complete after two days.

The concentration of hydrogen peroxide in the irradiated water was determined by measuring its absorption coefficients for ultraviolet rays. A Judd Lewis sector photometer and an Adam Hilger quartz spectrograph were used. The experimental procedure with these instruments is described elsewhere.[13] A low pressure hydrogen discharge tube was used for light source. The tube was built in the Minnesota laboratory. It operated continuously at 2100 volts a.c., 0.21

[13] Carl E. Nurnberger and L. Earle Arnow, J. Phys. Chem. **38**, 71 (1934).

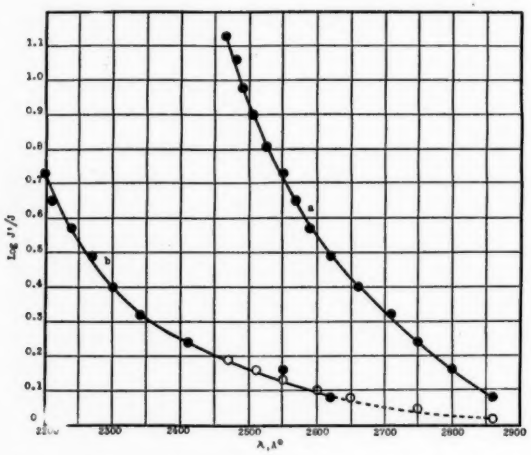

FIG 2. Ultraviolet absorption curves of hydrogen peroxide and of irradiated water. (a) 0.018 percent H_2O_2 in H_2O. 10 cm cell. (b) Irradiated H_2O in 10 cm cell.

ampere, and hydrogen pressure of approximately 3 mm of mercury. The easy and rapid alignment with the other optical instruments and the steady, intense, and continuous ultraviolet spectral emission of the tube are some of the advantages over the older under-water spark sources. The absorption of the cell and its contents was always measured relative to the absorption of pure water in a cell with quartz end plates.

The concentration of H_2O_2 in the water was determined by Beer's absorption law as expressed in the following equation,

$$c = (1/\epsilon d) \log (J'/J) \qquad (1)$$

where c is the number of H_2O_2 molecules per cubic centimeter, d is the length of the absorption cell, ϵ is the molecular absorption coefficient, and $\log J'/J$ is called the absorption factor. The latter was read directly from the photometer scale. Slight corrections were applied according to directions furnished by Hilger. The J and J' refer to the intensities of the incident and emergent light respectively.

RESULTS

Three photographic plates of the absorption of a known solution of H_2O_2 in the quartz cell (0.018 percent in 10 cm cell) were made for comparative purposes. Their average values are plotted in curve (*a*) in Fig. 2. The maximum deviation of $\log J'/J$ among the three plates was not greater than 0.05. The solid portion of curve (*b*) is the average of two plates exposed one immediately after the other of irradiated H_2O. Curve (*b*) is similar to the ultraviolet absorption curve of H_2O_2. If points on the known H_2O_2 curve are reduced by the factor 0.18, then the reduced points, indicated by the circles, all fall very close to curve (*b*). Since the concentration of H_2O_2 in curve (*a*) is 0.018 percent, then the concentration of absorbing substance in curve (*b*), presumably H_2O_2, is 0.018 percent $\times 0.18$, or 0.00327 percent. Both curves were obtained with the same absorption cell. Henri and Wurmer[14] found the absorption of H_2O_2 to be continuous. More recently Urey, Dawsey and Rice measured the absorption of H_2O_2 both for the liquid and gaseous states.[15] They also found the absorption to be continuous for wave-lengths of ultraviolet light from 3000 to 2200A. They determined the molecular absorption coefficients of carefully purified H_2O_2 for these wave-lengths. In Table I the molecular absorption coefficients of H_2O_2 and of the irradiated water may be compared. The latter were calculated by means of Eq. (1) and by assuming the concentration of H_2O_2 to be 0.00327 percent or 0.00149×10^{20} molecules per cc. Values for the longer wave-lengths were obtained by the extension of the experimental curve (*b*) through the reduced points of curve (*a*).

TABLE I. *The molecular absorption coefficients of H_2O_2 and of irradiated H_2O.*

	Molecular Absorption Coefficients		
λ, A	H_2O_2 Urey, Dawsey, Rice (a)	Author's H_2O_2 (*e*)	Irradiated H_2O (*e*)
2800	2.4×10^{-20}	2.0×10^{-20}	2.0×10^{-20}
2700	4.1	4.0	3.8
2600	6.9	6.7	6.8
2500	10.2	11.3	10.8
2400	14.7	17.6	16.8
2350	17.9		20.8
2300	22.0		26.1
2250	25.6		35.6
2200	28.9		48.3

[14] Henri and Wurmer, Comptes rendus **156**, 1012 (1913); **157**, 126 (1913).
[15] H. C. Urey, L. H. Dawsey and F. O. Rice, J. Am. Chem. Soc. **51**, 1371 (1929).

The agreement between Urey's and the author's coefficients for H_2O_2 is fairly good. The coefficients for the irradiated H_2O are very close to H_2O_2 for wave-lengths longer than about 2400A, but there is a decided increase for the shorter wave-lengths. The reason for this discrepancy is unknown. A portion of the difference may be due to the experimental methods, for there is a slight tendency in the author's coefficients for pure H_2O_2 to rise above Urey's for the shorter wave-lengths. Another possible explanation may be that impurities are liberated from the quartz surfaces under alpha-ray bombardment which absorb or scatter ultraviolet rays shorter than 2400A more than for the longer rays. Impurities are thought to be released from Pyrex and the increased conductivity of irradiated water is ascribed to them. Some sodium and calcium was found in earlier experiments.

The question might arise regarding the absorption of ultraviolet rays by radon and its decay products with the supposition that a part of the absorption of the irradiated H_2O is due to these materials. The absorption cannot be ascribed to radon. In 3.85 days 50 percent of the radon is destroyed, while the absorption factor as shown in the last column of Table II has maximum value in 4.74 days. Moreover, the rate of decrease is much slower than the disintegration rate of radon. It is doubtful if a part of the molecular absorption coefficient for wave-lengths shorter than 2400A can be attributed to the active deposits of radon. For of the most likely of these, the long life ones, only radium *E* might show absorption in this region. Radium *E* and bismuth might be expected to have similar absorption characteristics. Bismuth has not been measured for wave-lengths shorter than 2570A.

TABLE II. *A comparison of excess H_2 pressure and the absorption factor of the irradiated H_2O.*

Radon = 69.8 mc H_2O volume = 15.6 cc

Time days	H_2O Temp. °C	Gas Volume cc	Gas Pressures (mm)		Abs. factor Log J'/J λ2250
			$P_{O_2+H_2}$	P_{H_2}	
0	28.0	2.20	0	0	0
1.21	28.2	2.20	24	10	0.32
1.93	28.2	2.20	79	36	.40
2.72	28.0	2.20	153	68	.49
4.74	28.2	2.20		76	.53
5.64	28.2	2.20		77	.47
6.89	28.2	2.20		66	.41
9.68	28.2	2.20		62	.45
12.9	28.2	2.20		44	
13.7	28.2	2.20		42	.32

Table II contains the results of an experiment in which residual H_2 pressure and the absorption factor, $\log J'/J$, of the irradiated water were measured. Both increase, reach a maximum, and then decrease simultaneously in the course of the experiment. This sort of variation is consistent with Duane and Scheuer's hypothesis. However, no simple quantitative relationship exists between the excess H_2 and the absorption factor as was originally expected. On the contrary, the H_2 pressures at the beginning and end of the experiment were 10 mm and 42 mm respectively, while the absorption factor at these times had the same value, 0.32. Furthermore, in a period of 3.5 days the excess H_2 pressure increased 7.7 fold while the absorption factor for any specific wave-length increased only 1.7 fold. These figures indicate that either the excess H_2 cannot be due to the production of H_2O_2 alone or the method of measuring H_2O_2 does not give the true number of peroxide molecules. In order to carry the analysis further, the total maximum quantity of H_2O_2 molecules was calculated from the measured excess H_2 and from the measured absorption factor at 2250A. Assuming one H_2O_2 molecule for each excess H_2 molecule, the total maximum number of H_2O_2 molecules is given by

$$[(273\times77\times2.20)/(760\times301)]\times2.70\times10^{19} = 54\times10^{17},$$

where the part in brackets is the volume of H_2 reduced to standard pressure and temperature and 2.70×10^{19} is Loschmidt's number. From absorption measurements the total maximum number of H_2O_2 molecules is given by

$$(0.53/35.6\times10^{-20}\times10)\times15.6 = 23\times10^{17},$$

where 0.53 and 35.6×10^{-20} are the absorption factor and molecular absorption coefficient respectively for 2250A, 10 cm is the length of the absorption cell, and 15.6 cc is the volume of irradiated water. The lack of quantitative agreement between the two results may be due to the formation of clusters $(H_2O_2)_n$. This supposes that the absorption of ultraviolet rays by the cluster is less than the sum of the individual absorptions of its constituents and that,

TABLE III. *Spontaneous decrease of the absorption factor of a dilute aqueous solution of H_2O_2.*

Days	0	0.8	2.8	4.8	8.0
Log J'/J, λ2500	0.98	0.90	0.81	0.81	0.73

therefore, the second calculated value of total H_2O_2 is too small. The ratio $54\times10^{17}/23\times10^{17}$, which is approximately equal to 2, might be supposed to mean that n for the cluster is equal to 2, although there is no experimental evidence to support the supposition.

The decrease of H_2 has been assumed to occur as the result of the spontaneous decomposition of H_2O_2 and of alpha-ray decomposition. This assumption can be carried over now to explain the decrease in the absorption factor for a given wave-length. Since ultraviolet rays decompose H_2O_2,[14, 16] some of the reduction in (log J'/J) might be due to ultraviolet exposures during the photographing of the spectrum. The exposure times were short, so not much decomposition could be expected. However, some experiments were performed to determine how much change might occur in the absorption of a dilute solution of H_2O_2 on standing for several days at constant temperature without alpha-ray irradiation, but subjected to the usual ultraviolet ray exposures involved in the photographing of the spectrum. The results of a typical experiment are given in Table III. In 8 days the initial absorption had reduced approximately 25 percent. Most of this is most probably pure temperature or spontaneous decomposition. Under alpha-ray irradiation the maximum absorption decreased 40 percent in 9 days. Therefore, approximately one-fourth of the decomposition can be ascribed to alpha-rays and three-fourths to spontaneous decomposition.

Some oxygen is produced also with the hydrogen, for in each instance sparking of the gas reduced the pressure. After about the third day of the experiments, the combined O_2 and H_2 pressures were too large to be recorded by the manometer. However, explosions reduced the pressure to readable values. It is therefore concluded that alpha-rays do decompose air-free water and that hydrogen peroxide is formed. The mechanism of the reaction of alpha-rays and of x-rays on water appear to be unlike.

[16] Tian, J. Chem. Soc. **108**, 828 (1915); J. Soc. Chem. Ind. **35**, 114 (1916).

SUMMARY

1. The absorption spectrum of air-free water irradiated with alpha-rays has been found to be continuous beginning at approximately 2850A and extending to 2200A.

2. Similarities of the absorption curves of hydrogen peroxide and of irradiated water are noted. Points on the hydrogen peroxide curve when reduced by a common factor fall remarkably close to the irradiated water curve.

3. Molecular absorption coefficients of the irradiated water agree closely with the coefficients for H_2O_2 in the spectral region 2800–2400A; the agreement is not so good for shorter wave-lengths, which may possibly be due to absorption and scattering by impurities released from the quartz cell under alpha-ray bombardment.

4. Excess H_2 in the evolved gases and the H_2O_2 concentration in the irradiated water rise, reach a maximum, and decrease simultaneously.

5. Excess H_2 is not entirely due to formation of hydrogen peroxide as shown by quantitative determination of the total H_2O_2 from absorption measurements.

6. The major portion of the decomposition of H_2O_2 is spontaneous.

7. It is finally concluded that air-free water is decomposed by alpha-rays and that hydrogen peroxide is formed.

I wish to express my appreciation of the cooperation of Dr. W. K. Stenstrom of the Division of Biophysics and Cancer Institute, University of Minnesota, Minneapolis.

The Raman Spectra of Boron Trifluoride, Trichloride, and Tribromide. The Effect of the Boron Isotopes*

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The Raman frequencies $\nu_1\{1\}$, $2\nu_2\{2\}$, $\nu_3\{2\}$, and $\nu_4\{2\}$ for $BF_3(g)$, $BCl_3(l)$, and $BBr_3(l)$ were found to be 886 and 783, 1394, 1038 and 1105, 440; 471, 924, 958 and 996, 243; 279, 743, 806 and 846, and 151 cm^{-1}, respectively. The assignment of frequencies was determined by polarization experiments on BCl_3 and is confirmed for the three compounds by the results of a normal coordinate treatment. The doubling of ν_1 in BF_3 is ascribed to vibrational resonance between ν_1 and $2\nu_4$. The doubling of ν_3 in all three compounds is shown to be due to the presence of the two isotopes of boron B^{10} and B^{11}. A satisfactory assignment of the infrared frequencies of BCl_3 is made.

INTRODUCTION

THE Raman spectrum of boron trichloride has been reported by Bhagavantam and by Venkateswaran.[1] Cassie[2] has proposed an assignment for the infrared frequencies he observed for boron trichloride, but he assumed frequencies differing rather widely from the Raman frequencies as well as the presence of forbidden lines in the infrared spectrum.

We have reinvestigated the Raman spectrum of boron trichloride and report as well the Raman spectra of boron tribromide and boron trifluoride. In all three compounds a doubling of certain frequencies by the presence of the boron isotopes B^{10} and B^{11} is observed. The infrared spectrum of boron trichloride is satisfactorily explained by an assignment of frequencies which is confirmed by the results of a normal coordinate treatment.

The work on boron trifluoride was started at this laboratory in 1934 by Mr. S. T. Gross.

This and other similar investigations were assisted by a grant-in-aid of research to one of us (D. M. Y.) from the National Research Council. The boron tribromide used was prepared as an N.Y.A. project by Mr. David Pressman.

GENERAL THEORETICAL CONSIDERATIONS

The shape of the boron trichloride molecule is rather definitely shown to be that of a plane equilateral triangle with the symmetry D_{3h}. This follows from its zero dipole moment[3] and the results of electron diffraction experiments.[4] The results of the present investigation are in agreement with the assumption that the other boron trihalides also have the symmetry D_{3h}.

The BX_3 molecule then has the four symmetry modes of vibration indicated in Fig. 1. $\nu_1\{1\}$, $\nu_3\{2\}$, and $\nu_4\{2\}$ are allowed in the Raman effect with the depolarizations 0, 6/7, and 6/7, respectively.[5] Numbers in braces adjoining ν's are degeneracies. $\nu_2\{1\}$, $\nu_3\{2\}$ and $\nu_4\{2\}$ are active in the infrared. The selection rules for simple combinations and overtones obtained by the methods of group theory[6] are indicated in Table I.

The fact must be borne in mind that the presence of the isotopes of boron B^{11} and B^{10} in the approximate ratio of 4 to 1 will produce a doubling of those frequencies in which the boron atom moves appreciably. Thus in the Raman effect we should expect ν_3 and $2\nu_2$ each to appear as a doublet separated in frequencies by about 5 percent, and with the lower frequency about four times as intense as the higher. Analogous splits in frequencies should appear in the infrared spectrum with a ratio of extinction coefficients for the two components of 4 to 1. A normal coordi-

* Contribution No. 562 from the Gates and Crellin Chemical Laboratory of the California Institute of Technology.

[1] Bhagavantam, Ind. J. Phys. **5**, 73 (1930); Venkateswaran, ibid. **6**, 284 (1931).

[2] A. B. D. Cassie, Proc. Roy. Soc. **A148**, 87 (1935).

[3] E. Bergmann and L. Engel, Physik. Zeits. **32**, 425 (1931); H. Ulich and W. Nespital, Zeits. f. Elektrochem. **37**, 559 (1931); W. Nespital, Zeits. f. physik. Chemie **B16**, 153 (1932).

[4] L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936); private communication.

[5] E. B. Wilson, Jr., J. Chem. Phys. **2**, 432 (1934).

[6] E. Wigner, Gött. Nachr., 133 (1930); G. Placzek, *The Structure of Molecules* (Blackie and Son, London, 1932); L. Tisza, Zeits. f. Physik **82**, 48 (1933); E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934).

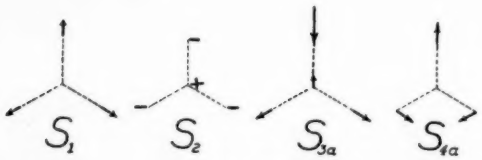

FIG. 1. Symmetry modes of the plane symmetrical BX_3 molecule.

nate treatment should enable one to predict the isotopic doubling of frequencies with greater accuracy.

EXPERIMENTAL

Boron trifluoride was prepared by treating ammonium fluoborate with concentrated sulfuric acid and heating. The reaction chamber was of glass, so silicon tetrafluoride was expected as an impurity. To prepare ammonium fluoborate, boric acid was treated with hydrofluoric acid in a copper beaker; the solution was neutralized with NH_4OH and concentrated by heating. Upon cooling the solution, NH_4BF_4 crystallized out. The BF_3 so prepared was fractionated repeatedly; the final product had a melting point of $-127\pm1°$, in good agreement with the value given in the literature. The Raman spectrum of the somewhat cloudy liquid under its own vapor pressure of 6 atmospheres at the temperature of a solid carbon dioxide alcohol bath was taken using a technique similar to that previously employed for phosphorus trifluoride.[7] The Raman spectrum of the gas at a pressure of six atmospheres was taken using the 2537A line of mercury as a source of radiation. The spectrum from the gas was much more satisfactory than that from the liquid.

Kahlbaum's C.P. boron trichloride (b_{760} 12.5°) was distilled into a Raman tube and sealed in without further purification. The Raman spectrum was obtained at room temperature from the liquid under its own vapor pressure. The polarizations of the two most intense lines were roughly determined. For this purpose[8] the mercury lamp was placed below the horizontal Raman tube with a series of parallel vanes of black cardboard between lamp and tube to insure that the light entering the tube was parallel. The scattered light from the Raman tube then passed successively through a half-wave plate for 4400A, a large Nicol prism with vertical axis, and a lens which focused the light on the 0.4 mm slit of the spectrograph. With the axis of the half-wave plate at an angle of 45° to that of the Nicol, only horizontally polarized light from the Raman tube passed through to the slit. When the axis of half-wave plate and Nicol were parallel, only the perpendicular component reached the slit. The advantage of this arrangement is that all light entering the spectrograph is vertically polarized so that there is no effect of selective transmission or reflection of the light from the slit or prism faces, in contrast to previously used arrangements. Two one-hour exposures were made on the same photographic plate with the two settings of the half-wave plate. Relative intensities of the lines in the two spectra were estimated visually and compared with the relative intensities of the Rayleigh lines which are known to be polarized.

Boron tribromide (b_{740} 90.1°) was prepared by passing bromine vapor over a mixture of boric oxide and carbon at 250°. It was carefully fractionated, the fraction used having a boiling point of $91.0\pm0.2°$. Difficulty was had in sealing the material in the Raman tube without the liberation of small amounts of bromine. The bromine was therefore removed by sealing a small amount of mercury in the Raman tube with the boron tribromide. The mercurous bromide, which was formed on shaking, settled out nicely and Raman spectra of the clear colorless liquid remaining were obtained.

TABLE I. *An addition table showing the selection rules for simple combinations and overtones of modes of vibration of BX_3 molecules.*

	$\nu_1\{1\}R$	$\nu_2\{1\}I$	$\nu_3\{2\}RI$	$\nu_4\{2\}RI$
$\nu_1\{1\}R$	R	I	RI	RI
$\nu_2\{1\}I$		R^*	R	R
$\nu_3\{2\}RI$			RI	RI
$\nu_4\{2\}RI$				RI

R indicates a Raman active combination; I indicates an infrared active combination.
* $3\nu_2$ is infrared active.

RESULTS AND ASSIGNMENT OF FREQUENCIES

The observed Raman frequencies and assignments are presented in Table II. We shall discuss

[7] D. M. Yost and T. F. Anderson, J. Chem. Phys. **2**, 624 (1934).

[8] The arrangement here described, which has been in use in this laboratory for some time, was developed by Dr. Fred B. Stitt of this laboratory. He will publish a more detailed account shortly.

first the more complete results for BCl_3 and proceed then to a discussion of BBr_3 and BF_3.

Boron trichloride

The results for boron trichloride agree with those obtained by Venkateswaran[1] with the exception that the broad band he observed at 947 cm^{-1} is resolved into a triplet. This group, consisting of a sharp line and two broad lines, is reproduced in Fig. 2. The depolarization of the 471 cm^{-1} line was found to be less than 0.25; it was therefore assigned to the mode ν_1. The depolarization of the line at 253 cm^{-1} was close to unity and it was therefore taken to be ν_4. The frequency ν_3 was taken to be the expected isotopic doublet 946, 989 cm^{-1}, the broadness of this pair distinguishing it from the sharp line at 902 cm^{-1}. The latter frequency was then assumed to be $2\nu_2$ whose weaker isotopic component is obscured by the 946 cm^{-1} frequency.

When we make the assignment of infrared absorption frequencies[2] indicated in Table III, we arrive at the values for the vibrational frequencies for $BCl_3(g)$ indicated in Table II. These frequencies differ only slightly from the Raman frequencies for $BCl_3(l)$. The agreement between observed and calculated frequencies is quite satisfactory with the exception of the assignment of the frequency 845 cm^{-1}. Its nearness to the frequency 834 cm^{-1} observed in the Raman spectrum of phosgene[9] and the fact that phosgene is often a by-product in the preparation of BCl_3 and difficult to separate from it, suggest that the presence of this band may be due to a trace of phosgene in the BCl_3 used. The infrared spectrum of phosgene has not been reported. The weaker isotopic components of $\nu_3+\nu_4$ and of $\nu_1+\nu_3$ are evidently too weak to be observed, while that of $3\nu_2$ is obscured by $\nu_1+\nu_3$ from $B^{11}Cl_3$. In other cases the estimated relative intensities of the bands are in accord with the relative abundancies of the boron isotopes. Unfortunately Cassie has not published data from which extinction coefficients could be calculated. The assignment of frequencies is confirmed by the results of the normal coordinate treatment which follows this section.

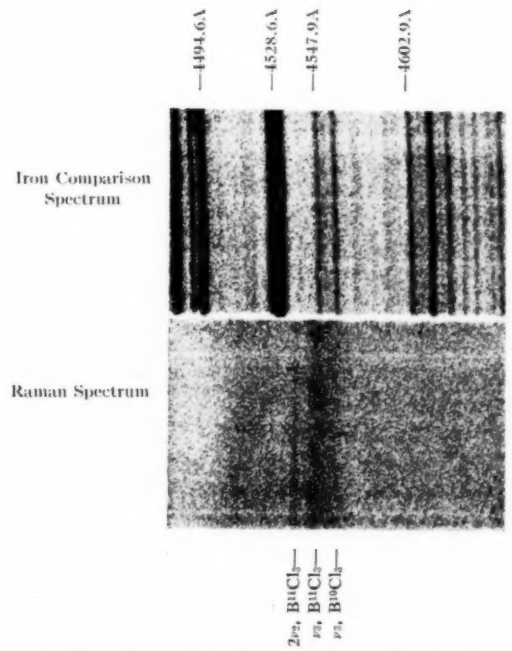

FIG. 2. The effect of the boron isotopes in the Raman spectrum of BCl_3.

TABLE II. *The Raman spectra of boron trifluoride, boron trichloride, and boron tribromide.*

SUBSTANCE	$\nu_1\{1\}$ (cm^{-1})	$2\nu_2\{1\}$ (cm^{-1})	$\nu_3\{2\}$ (cm^{-1})	$\nu_4\{2\}$ (cm^{-1})
$B^{11}F_3(g)$	886(7), 783(3)	1394($\frac{1}{2}$?)*	1038(1)	440(4*b*) ±25*
$B^{10}F_3(g)$	886(7), 783(3)	(1452)	1105($\frac{1}{2}$?)*	440(4*b*) ±25*
$B^{11}F_3(l)$	883(1), —	—	—	—
$B^{11}Cl_3(g)$†	471	924	958	243
$B^{10}Cl_3(g)$†	471	(966)	996	243
$B^{11}Cl_3(l)$	471(10)	902(3)	946(3*b*)	253(8)
$B^{10}Cl_3(l)$	471(10)	(943)	989(1*b*)	253(8)
$B^{11}Br_3(l)$	279(10)	743($\frac{1}{2}$)	806(3/4*b*)	151(8)
$B^{10}Br_3(l)$	279(10)	(780)	846($\frac{1}{2}$*b*)	151(8)

Numbers in parentheses adjoining frequency values indicate relative intensities. *b* = broad; all other lines are sharp. Numbers in braces adjoining ν's are multiplicities. Frequencies in parentheses are estimated.

* The assignment of these frequencies is provisional for $BF_3(g)$.

† Frequencies obtained from infrared data for $BCl_3(g)$.

[9] Kohlrausch, *Der Smekal-Raman-Effekt* (Julius Springer, Berlin, 1931).

Boron tribromide

The Raman spectrum of boron tribromide is very similar in appearance to that of boron

TABLE III. *The infrared spectrum of boron trichloride.*

$\nu_{obs.}$ (cm^{-1})	$\nu_{calc.}$ (cm^{-1})	Combination
714(4)	714	$\nu_1+\nu_4$
845(3)	834(*R*)	$COCl_2$ (?)
958(100)	958	ν_3, $B^{11}Cl_3$
996(50)	996	ν_3, $B^{10}Cl_3$
1206(2)	1201	ν_3, $B^{11}Cl_3+\nu_4$
1387(6)	1386	$3\nu_2$, $B^{11}Cl_3$
1429(6)	1429; 1452	$\nu_1+\nu_3$, $B^{11}Cl_3$; $3\nu_2$, $B^{10}Cl_3$
1912(2.5)	1916	$2\nu_3$, $B^{11}Cl_3$
1995(2)	1992	$2\nu_3$, $B^{10}Cl_3$

R = observed in Raman spectrum of $COCl_2(l)$.

TABLE IV. *Calculated force constants K, H, G, and K', calculated frequencies for trihalides containing B^{10}, and calculated internuclear distances B–X, for boron trihalides.*

SUBSTANCE	$K\times10^{-5}$ (dynes/cm)	$H\times10^{-5}$ (dynes/cm)	$G\times10^{-5}$ (dynes/cm)	$K'\times10^{-5}$ (dynes/cm)	$\nu_3B^{10}X_3$ calc. (cm^{-1})	$\nu_3B^{10}X_3$ obs. (cm^{-1})	$\nu_4B^{10}X_3$ calc. (cm^{-1})	$\nu_4B^{10}X_3$ obs. (cm^{-1})	B–X calc. (A)	B–X obs. (A)
$BF_3(g)$	4.24	0.60	0.88	1.73	1080	1105(?)	416	416*	1.49	1.42†
$BCl_3(g)$	3.30	0.276	0.434	0.653	1000	996	243	243	1.72	1.73
$BBr_3(l)$	2.50	0.252	0.270	0.61	843	846	151	151	1.85	1.87

* This value was assumed for ν_4, $B^{11}F_3$ in order to obtain real values for the constants.
† The sum of Pauling's double bond radii plus 0.04A was taken as an estimate for the B–F distance. See L. Pauling, L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **57**, 2705 (1935).

trichloride with $2\nu_2$ and the isotopic shift of ν_3 both appearing. By analogy with the assignment of the BCl_3 frequencies the assignment of frequencies indicated in Table II was made; confirmation is again obtained from the normal coordinate treatment.

Boron trifluoride

The Raman spectrum obtained from boron trifluoride is much more difficult to interpret. In addition to the frequencies listed in Table II, a line, doubtless due to the presence of SiF_4 ($\nu_1=800(10)$ cm^{-1}),[10] was observed at 801(4) cm^{-1}. The line assigned to ν_4 whose center is at 440 cm^{-1}, is 50 cm^{-1} in width. Its integrated intensity is therefore quite great. We then attribute the strong doublet, which appears as ν_1 in our assignment, to vibrational resonance between ν_1 and $2\nu_4$. Aside from the presence of impurities this appears to be the only reasonable possibility of accounting for the existence of both lines. If we introduce the perturbation term

$$H'=\gamma Q_1(Q_{4a}^2+Q_{4b}^2)$$

(where the Q's represent the normal coordinates and γ is a constant) in the potential energy expression one obtains the following energy levels from the solution of the secular equation:[11]

$$\lambda_1\{2\}=2\nu_4,$$
$$\lambda_2\{1\}=\tfrac{1}{2}[2\nu_4+\nu_1+\{(2\nu_4-\nu_1)^2+8P^2\}^{\frac{1}{2}}],$$
$$\lambda_3\{1\}=\tfrac{1}{2}[2\nu_4+\nu_1-\{(2\nu_4-\nu_1)^2+8P^2\}^{\frac{1}{2}}].$$

We should expect λ_2 and λ_3 to appear, while the simple overtone λ_1 should be very weak in the Raman effect. P, the perturbation energy defined in the usual manner, has the value 35 cm^{-1} when it is assumed that $\nu_1=2\nu_4=835$ cm^{-1}. This value is of the usual order of magnitude for P. The assignment of other observed frequencies is confirmed by the rather satisfying results of the following normal coordinate treatment. An investigation of the infrared absorption spectrum of BF_3 would doubtless yield a unique assignment.

NORMAL COORDINATES; COMPUTATION OF ISOTOPIC SHIFTS IN FREQUENCIES

Normal coordinate treatments of the plane symmetrical AB_3 type molecule have been made by a number of authors.[12] We shall use the valence force potential function V with force constants chosen so that

$$\begin{aligned}2V=&K(\Delta R_1^2+\Delta R_2^2+\Delta R_3^2)\\&+HR_0^2(\Delta\alpha_{12}^2+\Delta\alpha_{23}^2+\Delta\alpha_{13}^2)\\&+GR_0^2(\Delta\beta_1^2+\Delta\beta_2^2+\Delta\beta_3^2)\\&+2K'(\Delta R_1\Delta R_2+\Delta R_2\Delta R_3+\Delta R_1\Delta R_3).\end{aligned}$$

R_1 is here the distance $A-B_i$ and R_0 is this distance when the atoms are at equilibrium positions. α_{ij} is the angle B_i-A-B_j while β_i is the angle made by the line $A-B_i$ with the B_3 plane. The frequencies are then given by the equations:

$$m\lambda_1-K-2K'=0,$$
$$mM\lambda_2-(3m+M)G=0,$$
$$m^2\lambda_{3,4}^2-\{\tfrac{1}{2}(K-K')(3m/M+2)+H(9m/2M+3)\}m\lambda_{3,4}+H(K-K')(9m/M+3)=0.$$

Using the vibrational data for the boron trihalides containing the isotope B^{11} we have determined the various force constants with the

[10] D. M. Yost, E. N. Lassettre, and S. T. Gross, J. Chem. Phys. **4**, 325 (1936).
[11] T. F. Anderson, J. Chem. Phys. **4**, 161 (1936).
[12] D. M. Dennison, Phil. Mag. **1**, 195 (1926); F. Lechner, Wien. Bericht **141**, 633 (1932); J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 630 (1934); J. Rosenthal, Phys. Rev. **47**, 235 (1935). We have applied in part the results of Howard and Wilson in our treatment.

results indicated in Table IV. It is interesting to note that the constant G, usually assumed equal to H in the treatment of pyramidal type molecules, is nearly equal to H for heavy halogen atoms, but is considerably greater than H for light halogen atoms bound to the central boron.

Using these force constants we have calculated the frequencies ν_3 and ν_4 to be expected for the compounds containing the B^{10} isotope. The results agree well with the observed values as indicated in the table. The fact that the frequency ν_4 has little isotopic shift indicates that the symmetry modes are very nearly the normal modes in these cases.

Finally in Table IV, columns 10 and 11 are presented values of the internuclear distances calculated directly from the values of K by Badger's rule.[13] The agreement with the internuclear distances determined by electron diffraction experiments[4] is much better than would have been expected, judging from the experience of previous investigators.

[13] R. M. Badger, J. Chem. Phys. **2**, 128 (1934); **3**, 710 (1935).

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The Entropy of Carbon Tetrachloride

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A new calculation of the entropy of carbon tetrachloride has been made from Raman spectra and electron diffraction data. The effect of the isotopes of chlorine has been investigated. A new value of the calorimetric entropy has been computed from recent (and in part unpublished) thermal data. The agreement of the entropies is sufficiently good as to leave little reason to doubt the validity of the spectroscopic calculations.

SOME time ago Yost and Blair[1] noted a difference of about three entropy units between the entropy of carbon tetrachloride calculated from the existing thermal data[2] and a value of the entropy which they calculated from spectroscopic data by statistical methods. Assuming that the thermal data were substantially correct, they suggested that the discrepancy arose in the statistical calculation from uncertainty about the vibrational states of the molecule. The purpose of their note was to point out the dubious value, in their opinion, of spectroscopic entropy calculations made on the basis of the customary assumption that molecular vibrations are quasi-harmonic. In view of the good spectroscopic data available and the straightforward interpretation of the vibrational structure of carbon tetrachloride, it seemed to us unlikely that uncertainties of the sort suggested by Yost and Blair could account for the discrepancy between the thermal and spectroscopic entropies. Rather it appeared that the difficulty probably lay in the experimental thermal data. We have had put at our disposal some new unpublished heat capacity data for carbon tetrachloride. Furthermore we have made a new calculation of the statistical entropy, thoroughly investigating several possible sources of the disagreement. The theoretical and calorimetric data have been found to agree well within the limits of the probable experimental error in the latter.

[1] Yost and Blair, J. Am. Chem. Soc. **55**, 2610 (1933).
[2] Latimer, J. Am. Chem. Soc. **44**, 90 (1922).

STATISTICAL ENTROPY

It appeared worth while to refine the statistical computations by taking into account the isotopes Cl^{35} and Cl^{37}. The presence of these isotopes creates five different isotopic configurations for carbon tetrachloride, and the final value of the entropy has been obtained from the entropies of the configurations. It is to be remarked that the symmetry numbers of the various configurations are not uniformly twelve. At first sight, this variance in symmetry number might be thought

to affect the entropy considerably. However, because the isotopic ratio ordinarily remains fixed (i.e., no separation of isotopes occurs), the effect of isotopes on symmetry number may be disregarded. This neglect may be briefly justified as follows:

The only term in the entropy expression containing the symmetry number is of the form[3]

$$\frac{X!Y!Z!}{N_1!N_2!\cdots\sigma_1^{N_1}\sigma_2^{N_2}\cdots}, \tag{1}$$

which occurs in the expression for the γ-weight of the gas whose entropy is being calculated. In (1) the symbols X, Y and Z denote the actual numbers of the various atoms which have combined chemically to form the different kinds of molecules which make up the gaseous system. These molecules, the actual numbers of which are denoted by N_1, N_2, $\cdots$, possess, respectively, the symmetry numbers σ_1, σ_2, etc. In a mole of gaseous carbon tetrachloride, for example, there will be N carbon tetrachloride molecules ($N=6\times10^{23}$) which are made up of X carbon atoms ($X=6\times10^{23}$) and Y chlorine atoms ($Y=24\times10^{23}$). Eq. (1) may be written for this system:

$$\frac{X!Y!}{N!\sigma^N}. \tag{2}$$

When the Y chlorine atoms are sorted into Y_1 Cl^{35} atoms and Y_2 Cl^{37} atoms, (2) becomes

$$\frac{X!Y_1!Y_2!}{N_1!N_2!\cdots N_5!\sigma_1^{N_1}\sigma_2^{N_2}\cdots\sigma_5^{N_5}}, \tag{3}$$

in which the subscripts of the N's denote the various isotopic configurations of carbon tetrachloride.

Taking the mole fractions of the several configurations to be those corresponding to purely fortuitous molecular formation from chlorine isotopes whose abundance ratio is Y_1/Y_2, we find that expressions (2) and (3) are numerically identical. That is to say, the presence of the isotopes may be neglected insofar as its effect on tetrahedral symmetry is concerned. Giauque and Overstreet[4] have proved this for diatomic molecules in a different but fundamentally equivalent way. Incidentally they have shown (reference 4, p. 1735) that at high temperatures (specifically, at 298°K), the formation of the isotopic configurations of Cl_2 is strictly according to chance.

Langseth[5] has obtained the Raman spectrum of carbon tetrachloride under high dispersion, and has observed vibrational frequencies for the three most prominent isotopic configurations. By utilizing these observed values in conjunction with the formulas of Rosenthal[6] for isotopic frequency shifts, a complete set of frequencies has been worked out. These frequencies, in reciprocal centimeters, are listed in Table I.

Isotopic type I is CCl_4^{35}, type II $CCl_3^{35}Cl^{37}$, etc. For certain of the configurations, the degenerate vibrations split into groups of frequencies. The frequency values listed for these vibrations are weighted means of the individual frequencies. In addition, the triply degenerate ν_3 happens to be split into a doublet because of accidental resonance with the sum of ν_1 and ν_4. The extent of the splitting is small enough, however, that no appreciable error is introduced into the entropy by using an average of the two doublet components. This average frequency is listed for ν_3 in Table I.

For the calculation of rotational entropy, the moments of inertia were obtained from the accurate electron diffraction data of Pauling and Brockway.[7] The value of the carbon-chlorine

TABLE I. *Frequencies and degeneracies.*

Isotopic Type	$\nu_1(1)$	$\nu_2(2)$	$\nu_3(3)$	$\nu_4(3)$
I	461.5	219.0	777	315.5
II	458.3	216.6	775	314.6
III	455.2	215.8	772	312.8
IV	452.1	215.0	769	311.4
V	448.9	212.8	767	310.2

[3] See Ehrenfest and Trkal, Proc. Sect. Sci. Amstr. **23**, 162 (1921), Eq. (20), p. 170. Similar expressions are reproduced in Tolman, *Statistical Mechanics* (Chemical Catalog Company, New York, 1927), Eq. (246), p. 127; and in Fowler, *Statistical Mechanics* (Cambridge, 1929), Eq. (292), p. 102. A quantum mechanical justification of the use of symmetry number at high temperatures (above 100°K) will be found in the discussion given by Mayer, Brunauer and Mayer, J. Am. Chem. Soc. **55**, 27 (1933).

[4] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

[5] Langseth, Zeits. f. Physik **72**, 350 (1931).

[6] Rosenthal, Phys. Rev. **46**, 760 (1934).

[7] Pauling and Brockway, J. Chem. Phys. **2**, 867 (1934); J. Am. Chem. Soc. **57**, 2684 (1935).

TABLE II.

Isotopic Type	Mole Fraction	Entropy at 298°K					Entropy at 348.5°K				
		Trans.	Rot.	Vib.	Total	Fraction	Trans.	Rot.	Vib.	Total	Fraction
I	0.3319	40.97	28.51	9.36	78.84	26.17	41.76	28.97	11.39	82.12	27.26
II	0.4215	41.01	28.55	9.43	78.99	33.30	41.80	29.02	11.46	82.28	34.68
III	0.2008	41.05	28.59	9.51	79.15	15.89	41.84	29.05	11.53	82.42	16.55
IV	0.0425	41.08	28.63	9.58	79.29	3.37	41.87	29.10	11.59	82.56	3.51
V	0.0033	41.12	28.67	9.67	79.46	0.26	41.91	29.14	11.67	82.72	0.27
Sum of Fractional Entropies						78.99					82.27
$-R \ln \sigma(\sigma=12)$						−4.94					−4.94
Net Entropy of CarbonTetrachloride:						74.05					77.33

distance was taken as 1.76A. In computing the fractions of the various isotopic configurations, the relative abundance of Cl^{35} and Cl^{37} was taken as 0.759 : 0.241. (See reference 4, p. 1737.)

Entropies calculated for 298° and for 348.5° are listed in Table II. The latter temperature, 1.4° below the boiling point, was selected because an accurate determination of the heat of vaporization at 348.5° has been made by Mathews. The entropy of vaporization could thus be found directly rather than by the somewhat less precise method of calculation from vapor pressure data. The net entropies for carbon tetrachloride are obtained by multiplying the total entropy for each configuration by the appropriate mole fraction, adding these fractional entropies together and subtracting $R \ln \sigma$ (4.936 E.U. when $\sigma=12$). The symmetry number of each configuration is taken as 12 in accordance with the conclusion drawn from expressions (2) and (3). Entropy due to nuclear spin has been neglected.

THERMAL ENTROPY

As part of a survey being made in this laboratory of the low temperature specific heats of a group of compounds which have hitherto been investigated down to liquid-air temperatures only, one of us (E. R. B.) and R. W. Blue have carefully measured the specific heats of carbon tetrachloride between 16° and 85°K. These measurements were made in a modified Nernst vacuum calorimeter by a technique patterned after that developed by Giauque and his associates. The heat capacities were determined at approximately five-degree intervals, a gold wire resistance thermometer being used for the measurement of temperature increments. The measurements showed not only that the low temperature heat capacity data cited by Yost and Blair were considerably in error but also that the high temperature data were probably unreliable, and furthermore that investigations at temperatures still lower than 16° might be desirable. Recently Mr. D. R. Stull has communicated to us some measurements of the heat capacity of carbon tetrachloride between 100° and 335°K which he has made in an improved form of calibrated heat conduction calorimeter.[8] These latter measurements probably contain random errors of the order of 1.5 percent. Detailed reports on these and other heat capacity studies made in this laboratory will be given subsequently by the workers responsible for them.

New determinations of the temperatures and heats of fusion and of transition have been made by Johnston and Long.[9]

A summary of the new heat capacity data is shown in Table III. The values were taken at even temperatures from the smoothed curve employed in making the entropy integration. The listed temperatures do not indicate the temperatures of actual measurements. The entropy calculation is given in Table IV. The heat capacity data were integrated graphically in the usual manner, the entropy below 10° being obtained from a T^3-extrapolation.

[8] Andrews, J. Am. Chem. Soc. **48**, 1287 (1926); Smith and Andrews, ibid. **52**, 3644 (1931).

[9] Johnston and Long, J. Am. Chem. Soc. **56**, 31 (1934).

TABLE III. *Heat capacity of carbon tetrachloride.* Calories per mole 0°C = 273.10°K.

T°K	C_p	T°K	C_p
Solid 1		*Solid 2*	
18	3.81	230	29.65
20	4.98	240	29.82
25	6.78		
30	8.09	*Liquid*	
40	10.07	260	31.68
50	11.32	270	31.31
60	12.45	280	31.00
70	13.70	290	30.60
80	14.80	300	31.04
* * * * *		310	31.63
100	16.68	320	32.19
120	18.50	330	32.78
140	20.14		
160	21.74		
180	23.51		
200	25.70		
220	28.12		

TABLE IV. *Calculation of the entropy of carbon tetrachloride.*

	298°K	348.5°K
0°–10°K, T^3-extrapolation[a]	0.25	0.25
10°–85°K, graphical (B & B) 16.21 85°–225.4°K, graphical (Stull) 20.08	36.29	36.29
Transition, 1080.8/225.4 (J & L)	4.79	4.79
225.4°–250.2°K, graphical (Stull)	3.08	3.08
Fusion, 577.2/250.2 (J & L)	2.31	2.31
250.2°–298°K, graphical (Stull)	5.45	5.45
298°–348.5°K, graphical	—	5.05[b]
Vaporization	25.94[c]	20.55[d]
Compression: R ln 114.5/760	−3.76	—
R ln 730/760	—	−0.08
Calorimetric entropy, cal./deg./mole	74.35	77.69
Spectroscopic entropy, this research	74.05	77.33
" " Yost & Blair	74.3	

[a] $C_p = aT^3$, where $a = 0.75 \times 10^{-3}$ cal./deg.^{4}/mole.
[b] Heat capacity data extrapolated graphically from 334°K.
[c] Int. Crit. Tab., Vol. III, p. 215.
[d] J. H. Mathews, J. Am. Chem. Soc. **48**, 562 (1926).

CONCLUSION

At low temperatures the heat capacity of carbon tetrachloride is considerably larger than the earlier measurements indicated. The discrepancy between the value of the thermal entropy cited by Yost and Blair and the spectroscopic entropy is thus to be ascribed to erroneous heat capacity data, chiefly below 70°K. It is difficult to estimate closely the accuracy of the value of the thermal entropy given here. The entropy below 20°K may be in error by as much as 0.15 E.U. In the region between 80° and 140° there remain uncertainties in the heat capacity data which could conceivably affect the entropy to the extent of 0.5 E.U. We believe, however, that the value of the thermal entropy may be safely considered to be within 0.7–0.8 E.U. of the true value.

To bring the spectroscopic entropy into exact agreement with the present value of the thermal entropy requires a symmetry number in the neighborhood of 10. This number is uncertain by two or three units because of the doubt about the heat capacity data. It is therefore seen that accurate thermal data are a prime necessity for a valid determination of σ. A trustworthy evaluation of σ is also dependent upon a satisfactory analysis of vibrational frequencies and upon freedom of the thermal entropy of the crystalline state from such effects as have been studied by Giauque and his associates.[10] For carbon tetrachloride, however, the vibrational analysis is assuredly correct, and it appears likely that the entropy of the crystal is free from orientation effects of the sort found in N_2O, CO and H_2O. We believe therefore that the agreement which we have obtained between thermal and statistical entropies indicates the reliability of calculations based on the sort of spectroscopic data we have utilized.

Acknowledgment is made to Mr. D. R. Stull for permission to use and publish in part data obtained by him, and to Professor J. E. Mayer for constructive criticism of the statistical discussion.

[10] Giauque and Johnston, J. Am. Chem. Soc. **50**, 3221 (1928). Clayton and Giauque, ibid. **54**, 2610 (1932). Blue and Giauque, ibid. **57**, 991 (1935).

Absorption Spectra of the Vapors of Twelve Alcohols and of Nitric Acid in the Region of the O−H Harmonic Band at λ9500*

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The absorption spectra of the vapors of twelve alcohols and of nitric acid have been investigated by photographic methods in the region λλ9450–9850. In each case a strong harmonic band of the O−H vibration was found. In the primary alcohols and in *o*-chlor phenol the O−H vibration was found to split into two components, a possible explanation for which is briefly discussed. In the bands of certain other substances a considerable complexity of structure was observed which is attributed either to a free rotation or a torsional vibration of the hydroxyl hydrogen with respect to the remainder of the molecule. Systematic shifts in the frequency of the O−H vibration with changes in the structure of the alcohol molecule were found.

INTRODUCTION

THE authors have recently become interested in the study of the spectra of molecules in which there is the possibility of either a free rotation of two parts of the molecule with respect to each other, about a certain bond, or at least of a restrained rotation or torsional vibration. The theory of spectra of this type is in a very undeveloped state and its extension to other than the simplest cases appears to be extremely difficult. Consequently the best method of attack at present appears to be the comparative study of a number of similar substances in an attempt to find empirical relationships and if possible to develop a qualitative semi-classical picture which will account for the observed facts.

Substances containing the hydroxyl radical are especially convenient for study in the photographic infrared since the O−H harmonic bands appear with great intensity and the vibration which gives rise to them is nondegenerate in the ordinary sense though, as will be seen, it occasionally splits into two components. In a recent paper[1] we have described two bands of methyl alcohol which have a complex structure evidently due to the type of degree of freedom above mentioned. The present paper extends the investigation to eleven other alcohols and to nitric acid, all of which were studied in the vapor state in the region λλ9450–9850, in which bands corresponding to the transition 0→3 in the O−H vibration are found.

The next lower harmonic of the O−H vibration in certain of these substances, when in dilute solution in carbon tetrachloride, has been examined by Wulf and Liddel.[2] Our results are in agreement with those of these workers insofar as a comparison may be made. However, since we have worked with the substances in the vapor state and with high dispersion we have uncovered considerable complexity of structure which is wiped out in the liquid condition.

EXPERIMENTAL

The experimental procedure was essentially the same as that used in the investigation of methyl alcohol,[1] except that the ten-foot absorption tube of glass was used in each case. Exploratory photographs were taken with a glass spectrograph which has a dispersion of 70A per mm at λ9000, to locate the absorption region in each case. A more intensive examination was then made with the grating spectrograph which has a dispersion of about 2.5A per mm. The final measurements were made, in most cases, on microphotometer curves using water vapor lines as references. Because of the weakness of water lines at λ9800 the *B* band of *o*-chlor phenol and the band of nitric acid were measured with reference to iron lines in the second and third orders.

The alcohols investigated were of the highest purity which we could conveniently obtain. They were first dried with anhydrous sodium sulfate

* This investigation is a part of a program of research made possible by a grant to one of us (R. M. B.) from the Penrose Fund of the American Philosophical Society, for which it is desired to express appreciation.

[1] Badger and Bauer, J. Chem. Phys. **4**, 469 (1936).

[2] Wulf and Liddel, J. Am. Chem. Soc. **57**, 1464 (1935).

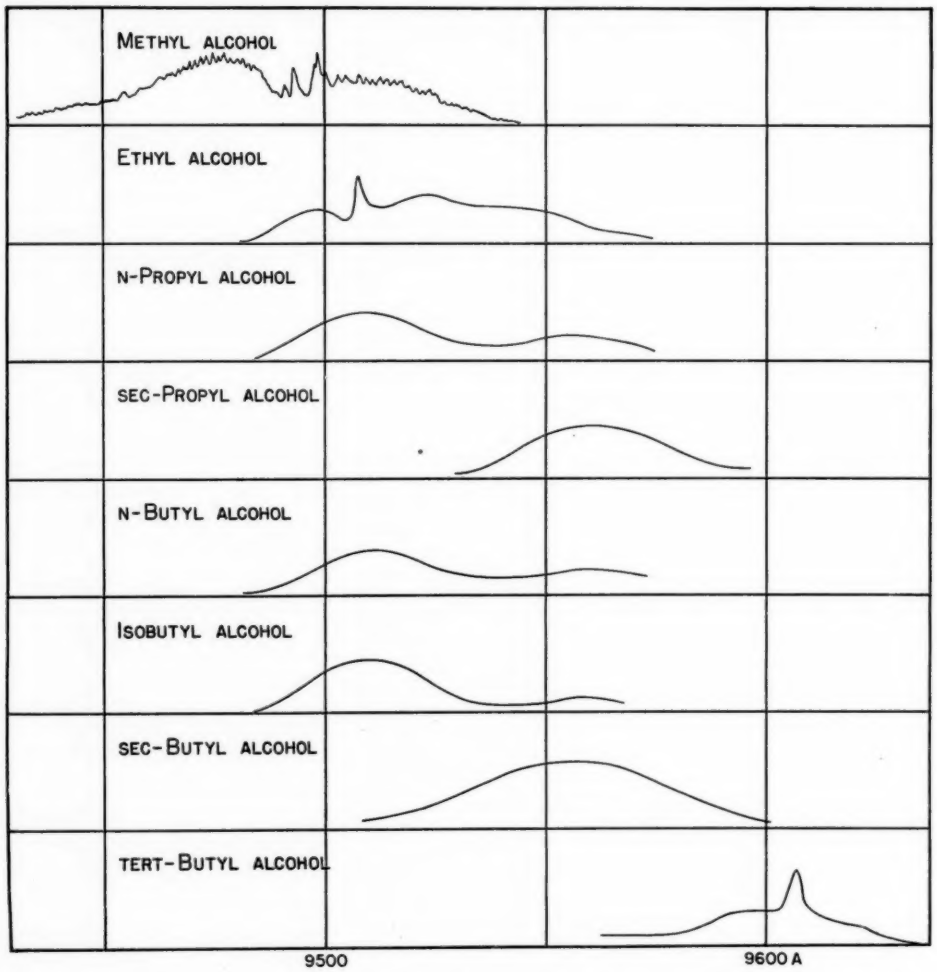

FIG. 1. Microphotometer curves of the O—H harmonic bands in the vapors of eight aliphatic alcohols in the λ9500 region.

or sometimes with metallic sodium, and were then fractionated in a four-foot bead-filled column when a sufficient quantity of the material was available. In the case of *o*-chlor phenol we took particular care that no appreciable amount of phenol was present as impurity. From comparisons of the freezing and boiling points of our substance with those of a sample to which a trace of phenol had been added we estimate that the maximum amount of this impurity which could have been present was less than 2 percent.

The nitric acid was prepared by the action of concentrated sulfuric acid on potassium nitrate. A rather pure product was apparently obtained but after a short time in the heated absorption tube some decomposition took place and the tube became opaque except to the red and longer wave-lengths. The oxides of nitrogen produced by the decomposition absorb extremely weakly in the region in which we were interested and did not interfere in any way.

The spectra of all the substances reported on were obtained at pressures between one-half and one atmosphere.

The results of the investigation are set forth in Figs. 1 and 2, in which are shown microphotometer tracings of the plates taken with high dispersion. In Fig. 2 the *A* band of *o*-chlor phenol has been reproduced on a considerably enlarged vertical scale to show its shape more clearly. We estimate this band to have between one-seventh and one-eighth the intensity of the

TABLE I. *Absorption maxima in the O—H harmonic bands of the vapors of eight aliphatic alcohols in the region λ9500.*

Type of alcohol	Example	Formula	Absorption maximum λ (A)	Absorption maximum ν (cm⁻¹)
—	Methyl	CH_3OH	9493.1 (Q?)	10531.1
primary	Ethyl	CH_3CH_2OH	A 9499	10524
			A 9507.8 (Q)	10514.8
			A 9524	10497
			B (9547)	(10472)
	n-Propyl	$C_2H_5CH_2OH$	A 9510	10512
			B 9557	10461
	n-Butyl	$C_2H_5CH_2CH_2OH$	A 9512	10510
			B 9560	10457
	iso-Butyl	$(CH_3)_2CHCH_2OH$	A 9510	10512
			B 9559	10458
secondary	*sec*-Propyl	$(CH_3)_2CHOH$	9561	10456
	sec-Butyl	$C_2H_5CH(OH)CH_3$	9557	10461
tertiary	*tert*-Butyl	$(CH_3)_3COH$	9607.3	10405.9

TABLE II. *Absorption maxima in the O—H harmonic bands of the vapors of some other substances.*

Substance	Formula	Absorption maximum λ (A)	Absorption maximum ν (cm⁻¹)
Allyl alcohol	$H_2C:CHCH_2OH$	9566	10451
Ethylene glycol	$HOCH_2CH_2OH$	9547 ?	10471
		9610 ?	10403
Phenol	C_6H_5OH	9553.4	10464.6
		9559.5	10457.9
		9565.0 (Q?)	10451.8
		9569.6	10446.8
o-Chlor phenol	C_6H_4ClOH	A 9573	10443
		B 9812	10189
Nitric acid	$HONO_2$	9819	10183
		9826	10174
		9829.9 (Q)	10170.2
		9838.9	10160.9
		9846.1	10153.5

B band at 160°C. The microphotometer curves have been corrected for the superposed water spectrum which could not be eliminated entirely except in the longer wave-length portion of the region investigated. This correction may be a trifle uncertain in the case of methyl alcohol, the only substance which showed any resolvable rotational structure of the ordinary sort, and possibly also in phenol, though it cannot be greatly in error. In all other cases it could be made very easily owing to the broad, continuous character of the bands and the extreme sharpness of the water lines.

Microphotometer curves are not given for allyl alcohol and ethylene glycol. Our plates of the former substance are not entirely satisfactory though it seems quite clear that there is but one absorption region which is similar to that of the secondary alcohols. Ethylene glycol absorbs very weakly indeed and we were unable to get satisfactory plates under high dispersion. The measurements given were made on a low dispersion plate and the accuracy is not great. There appear to be two maxima of absorption though this is not quite certain.

DISCUSSION

The aliphatic alcohols

As will be seen in Fig. 1, the spectra of the four primary alcohols studied which contain the group CCH_2OH, are very similar. They all possess a strong absorption region around λ9510, and another around λ9560 which is much weaker

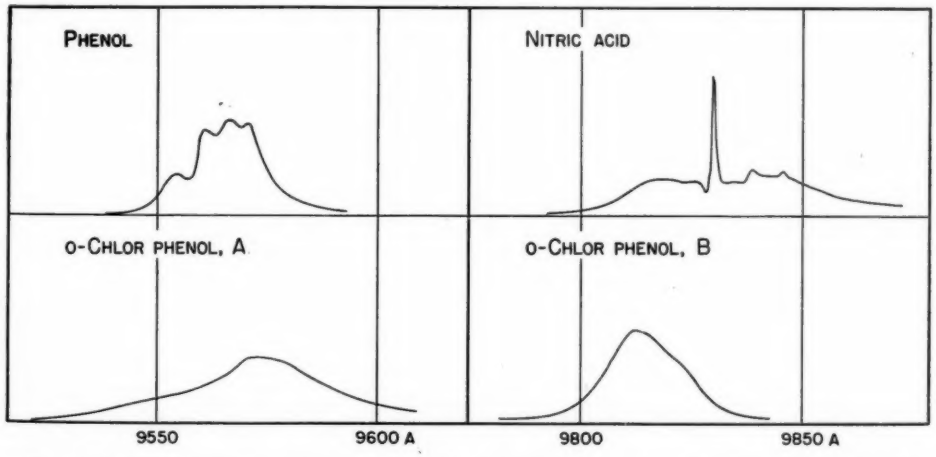

FIG. 2. Microphotometer curves of the O—H harmonic bands in the vapors of phenol, *o*-chlor phenol and nitric acid. The vertical scale of the *A* band of *o*-chlor phenol is enlarged about five times relative to that of the *B* band.

but quite definitely present. Ethyl alcohol shows some special features for which a possible explanation is suggested below. The spectra of the two secondary alcohols examined are practically identical. In each case there is a single absorption region at about λ9560. Unfortunately we have only one example of a tertiary alcohol, which is in some respects a special case. We hope later to study the amyl alcohols but this will necessitate some changes in our experimental arrangements. It is possible that some of the amyl alcohols will show anomalies, which indeed seems to be indicated in *sec*-isoamyl alcohol by the work of Wulf and Liddel.[2]

It is interesting to note that as each of the hydrogen atoms of the methyl group in methyl alcohol is replaced by an aliphatic radical the major absorption region shifts by a more or less definite amount. Due to the complex structure of the methyl alcohol band and the uncertainty as to what we shall regard as its center, it is difficult to say what this shift is as the first hydrogen is replaced, but in the second and third steps it is practically constant and amounts to about 54 cm^{-1}. This shift cannot be entirely or even largely a mass effect due to the similarity of the spectra of all the primary alcohols, and likewise of the secondary alcohols. It is impossible to say what shift should be expected from the mass effect alone since a normal coordinate treatment of the alcohols would be practically impossible at present. In any case it appears reasonable to us to attribute the effect largely to a change in the strength of binding which is indicated by the differences in reactivity, heats of combustion, etc., of the primary, secondary and tertiary alcohols.

It is interesting that the absorption band of allyl alcohol lies very close to those of the secondary alcohols. Since the structure of this substance appears to be well established by chemical evidence it would appear that there must be a rather large interaction between the O−H bond and the double bond.

The weakness of the absorption found in ethylene glycol is possibly due to chelation or association.

Phenol and *o*-chlor phenol

The O−H frequency in phenol lies between those of the secondary and tertiary alcohols, which is about what one would expect. The structure of the band observed is rather complex and resembles in some respects those found for methyl alcohol, though it is more compressed. When a chlorine atom is introduced into phenol in the *ortho* position the O−H band splits into two components, the stronger of which is shifted about 260 cm^{-1} and the weaker about 10 cm^{-1} to the low frequency side of the phenol band. These two bands of *o*-chlor phenol have a similar appearance. Much of the complexity of structure found in phenol has been lost though there is some indication that each of the component bands may consist of two branches of unequal intensity.

An explanation of the splitting of the O−H frequency in *o*-chlor phenol has been given by Pauling[3] who believes that the two potential minima which would be encountered if the hydroxyl hydrogen were to rotate are sufficiently deep to prevent free rotation and to keep the molecule in either of two possible configurations in which the O−H vibration has somewhat different frequencies.

Nitric acid

Our work on the vapor definitely establishes the presence of an hydroxyl group in the undissociated nitric acid molecule. In pure liquid nitric acid the O−H frequency should certainly be very weak due to the possibility of hydrogen bond formation. In one case it has been reported as present,[4] though somewhat doubtful, in the Raman spectrum of the liquid, but other workers have failed to find it. However, six other Raman lines[4, 5] appear to be well established as characteristic of the undissociated molecule, namely those with frequency shifts of approximately: 607, 667, 916, 1292, 1665 and 1687 cm^{-1}. In

TABLE III. *Provisional correlation of the frequencies of the nitrate ion with those of the undissociated nitric acid molecule.*

Nitrate ion	Nitric acid molecule
1071 (valence vibration, non-degenerate)	1292
1389 (degenerate)	1665 1687
726 (degenerate)	607 667
830 (bending out of plane)	916

[3] L. Pauling, J. Am. Chem. Soc. **58**, 94 (1936).
[4] Dadieu and Kohlrausch, Naturwiss. **19**, 690 (1931).
[5] Aderhold and Weiss, Zeits. f. Physik **88**, 83 (1934).

comparing these with the frequencies of the nitrate ion as found in crystals[6] and in aqueous solutions of the nitrates[7] and of nitric acid[5] it appears that there is a certain correlation. However, there is a considerable frequency shift and the two degenerate frequencies of the nitrate ion appear to split in nitric acid, showing the absence of a threefold axis.

In Table III is given a provisional assignment of frequencies in relation to those of the nitrate ion.

This leaves two vibrations still to be assigned, both of which are bending motions which chiefly involve the hydrogen atom. Owing to association in the liquid, which must greatly affect their character, they will have to be investigated in the vapor condition or in dilute solutions of the acid in some nonionizing solvent. One of these vibrations may be of moderately high frequency, the other may border on free rotation and we believe it is responsible for the complex structure of the band at λ9830 which we have investigated.

Methyl alcohol, *tert*-butyl alcohol, phenol and nitric acid

The spectra of these substances all possess a relatively great complexity and have certain features in common, in particular the presence of one or more Q branches. It appears to us that in these cases we have a closer approach to free rotation of the hydroxyl hydrogen than in the other substances which we have studied, which may be responsible for the particular type of structure. A further important similarity is that each of the molecules, exclusive of the hydroxyl hydrogen, has an axis of symmetry about which this atom will rotate in case it is free to do so. In methyl alcohol and *tert*-butyl alcohol this axis is threefold, in the other two cases it is twofold.

The two absorption regions of the primary alcohols

It is possible that the two absorption regions of the primary alcohols may have an explanation similar to that applicable to *o*-chlor phenol. Pauling's interpretation of this last case has been mentioned. It is certainly very suggestive although it is not clear to us that it is complete,

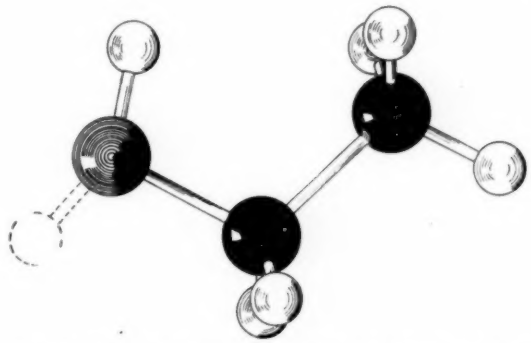

FIG. 3. Model of the ethyl alcohol molecule showing two orientations of the hydroxyl hydrogen which may correspond to minima of potential energy.

especially in view of the unexpected complexity of the phenol band. However, it appears that in ethyl alcohol there are two orientations of the hydroxyl hydrogen which may well correspond to potential minima, as shown in Fig. 3. In one of these the environment of this atom will be similar to that in methyl alcohol, in the other it will be considerably different. Furthermore, in the former orientation the change in electric moment will have a large component in the direction of the axis of least moment of inertia, in the latter it will be nearly perpendicular to this axis, which may account for the presence or absence of a Q branch in the two absorption regions, respectively.

In the higher primary alcohols the hydrocarbon chain is much more likely to be found in an extended than in a coiled condition. As evidence for this statement we may mention the well-known measurements on the thickness of surface films of polar molecules. This being the case the situation with regard to the hydroxyl hydrogen will be very similar in most primary alcohols.

In the secondary alcohols it is rather more difficult to see what configurations may correspond to potential minima. Since the observed spectrum is a rather broad band with a single maximum and no observable structure it may be that the environment of the hydroxyl hydrogen is not very different in the various positions it may occupy.

The authors plan to extend the type of investigation here described to the study of a series of amines and similar compounds, including hydroxylamine and hydrazine.

[6] A. C. Menzies, Proc. Roy. Soc. **A134**, 265 (1931).
[7] P. Grassman, Zeits. f. Physik **77**, 616 (1932).

Hydrogen Ion Concentration and the Behavior and Measurement of Monomolecular and Polymolecular Films on Water

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(Received July 30, 1936)

1. INTRODUCTION

IN view of the great importance of hydrogen ion concentration in chemical equilibria in chemical and biological systems, several attempts have been made to examine the effect of the hydrogen ion concentration of the substrate upon the behavior of monomolecular films of polar substances on water surfaces. Up to the present time the results obtained by various investigators possess little more than qualitative significance for one or more of the following reasons:

1. Substances chosen as showing the most marked effects, and hence studied in detail, such as proteins, have been of a doubtful purity and uncertain chemical constitution.

2. In many cases there is considerable doubt that a true monomolecular film was obtained; the films may have consisted of polymolecular aggregates enmeshed in a monomolecular layer.

3. Capillary-active buffers, such as citrate, acetate and borate, have been used and the results have obviously been affected by the adsorbed film of the buffer constituents.

4. The rate of compression of the films has been purely arbitrary. No detailed analysis of the effect of the rate of compression has yet been made by any investigator in the field. As shown below this is very important since new phenomena appear upon slow compression.

These objections indicate that a reexamination of the phenomena under controlled conditions should yield results of more quantitative character and of value in the solution of biological problems. For this reason an investigation was undertaken to determine if there exists any simple relationship between the character of the force-area curve and the state of ionization of the film. The above objections were avoided as follows:

1. The substance used was myristic acid, a crystalline material of high purity and definite chemical composition, which yielded expanded films which withstand considerable compression whether spread from solvent or from the crystals.

2. The results of many investigators have left no doubt that the film obtained from myristic acid is truly monomolecular, at least when first spread.

3. Noncapillary active substances, such as hydrochloric acid, potassium phosphate, sodium hydroxide and sodium bicarbonate were used in the preparation of the substrates.

4. The rate of compression of the film was varied, with equal time intervals between points, to determine the effect of the rate on the character of the *F–A* curve. A suitable rate was chosen to allow equilibrium to be established after each pressure increment, yet such as not to allow the film to dissolve more than was necessary.

5. An apparatus of high precision and an improved technique of spreading were employed since small differences in behavior might easily be overlooked with apparatus of the usual degree of precision.

The work done thus far indicates some of the difficulties still to be overcome in a problem of this character, and seems to point to a more desirable method of attack. Inasmuch as small differences may be important, a new improved film balance of high precision was constructed and an improved technique of spreading from a volatile solvent was employed. These are described in detail.

2. APPARATUS AND PROCEDURE

The apparatus consists essentially of a trough of glass as used by Agnes Pockels,[1] together with an improved torsion balance, which is a modification of that used by Adam.[2] In Fig. 1, the trough *ABA* may be indicated as *ABA*1, and the balance as *G*1. This abbreviated system of designation is followed throughout the paper.

The trough, as indicated by the figure, is set on three adjustable supports of brass and amber (*O*1) inside a tight box of plate glass, with a heavily galvanized cold-rolled steel flat as a base, supported by screws which are used to adjust the level of the base. The glass box is inside a thermally insulated metal box, which serves as an air thermostat. In a later model this air thermostat is inside a water thermostat which totally incloses it except for a large enough opening in front to allow the trough to be removed.

[1] A. Pockels, Nature **43**, 437 (1891).
[2] N. K. Adam and G. Jessop, Proc. Roy. Soc. **A110**, 423 (1926).

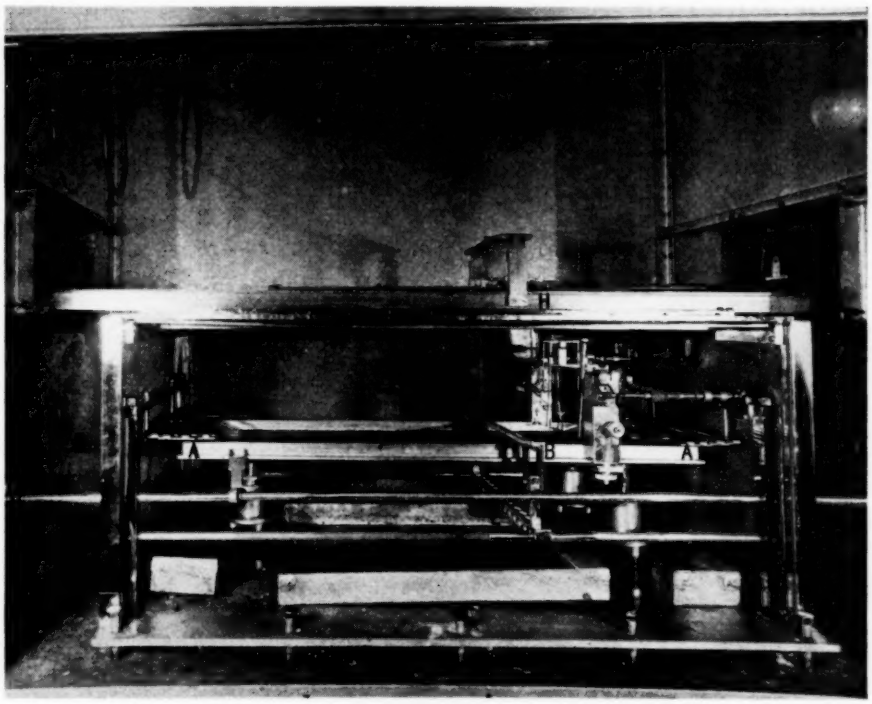

FIG. 1. Trough and film balance inside glass box with front removed. The copper netting is for electrical shielding. The outer box of metal is the air thermostat.

The trough $ABA1$ is filled with conductivity water, or with an aqueous solution with a known pH made from water free from organic matter. The film is held between a barrier of glass, the front end of which is at $B1$, and a float of phosphor bronze attached to the film balance. The glass barrier is moved by two forks, the front one at $B1$, attached to a slide $E1$ underneath the balance. The slide is driven by a screw of known pitch, which is turned by a wheel ($K2$) outside the right end of the thermostat. The number of whole turns of the screw is registered by the counter M, and the partial turns by marks on the wheel. By this means the position of the barrier may be read to 0.1 mm. Since all films examined are from 100 to 300 mm in length, the precision here is better than 0.1 percent.

Before the film is put on the surface of the water, and while the glass barrier is still on the left shelf at $A1$, the forks $B1$ are set in line with the film balance, and the surface of the water is swept by the use of paraffined brass sweepers which lie on the shelves at $A1$. To pick up a sweeper a handle outside the left end of the thermostat is pushed and turned. This moves the rods $DD1$ and the attached forks at $C1$. In this way any sweeper may be removed from the shelf, brought against the edge of the film balance without touching the surface of the liquid, and then lowered into the surface. The sweeper may then be moved along the surface to the corresponding end of the trough. The surface is thoroughly cleaned by several sweepings while the whole apparatus is kept closed. Also the right end of the trough, which has no film at the surface, may be swept at any time to determine if it has become contaminated.

A more sensitive method for the detection, but obviously not for the removal of uncleanliness, is to compress the contamination film against the float by the use of one of these barriers.

When desired the whole surface of the liquid may be swept by barriers from $A1$ before the film balance is lowered into its place.

The worm gear device which turns the end of the torsion wire is driven by the rod $G1$ which contains an insulating section of amber,

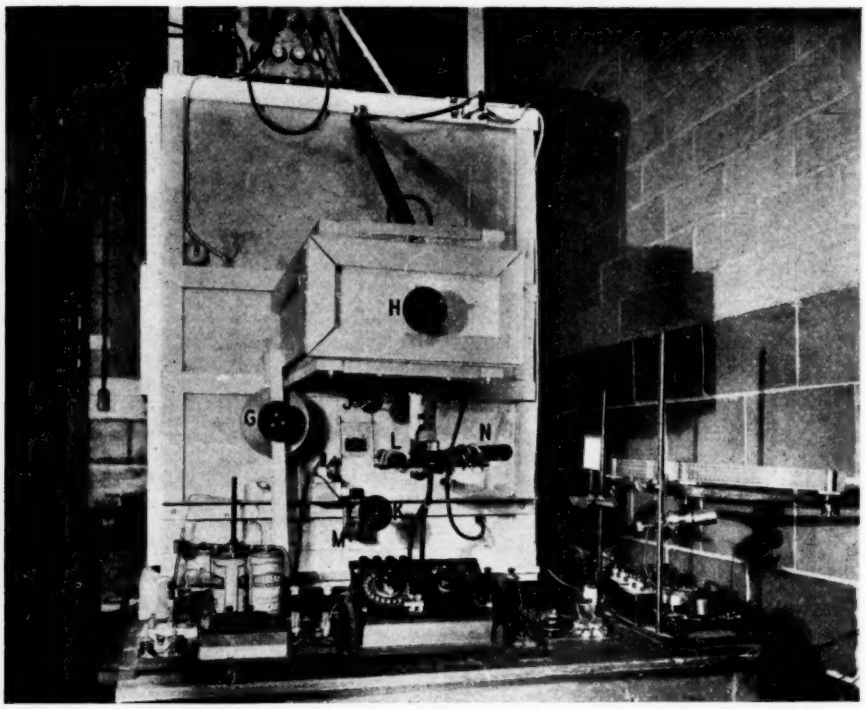

FIG. 2. Right end of air thermostat with controls for film balance, barrier, and electrodes (H). The controls for the sweepers are at the left end.

and is turned by the hard rubber disk at $G2$. The bright circle of brass at $G2$ has a graduated circle, read by a vernier on its edge. The circle and rod $J2$ are used to raise and lower the balance support shown in the photograph (Fig. 3).

The telescope $L2$ is used to read the graduated scale in the mirror of the film balance, while that at $N2$ is used to read the graduated circle and vernier in the mirror.

The hard rubber circular disk $H2$ is used to turn a screw which moves a set of four or more electrodes supported in the brass cover $H1$ at the top of the glass box which incloses the apparatus. These electrodes are used to determine the surface contact potentials.

The electrical equipment in Fig. 2 is for the determination of the hydrogen ion concentration of the solution used in the trough. The apparatus used for the determination of the surface potential consists of a potentiometer, a Compton electrometer, and silver electrodes coated with polonium, as described by Harkins and Fischer.[3]

[3] W. D. Harkins and Fischer, J. Chem. Phys. 1, 852 (1933).

3. FILM BALANCE

The details of the film balance itself are shown in the photograph (Fig. 3) and the drawing (Fig. 4). The description, the letters of which refer to Fig. 4, gives particular attention to the improvements or changes which have been made in the new design.

The measurement of film pressure is carried out, as heretofore, by a determination of the torque in the torsion wire $A4$ which is necessary to return the float $B4$ to its zero position.

1. The gold ribbons $C4$ are 3 mm high, 0.01

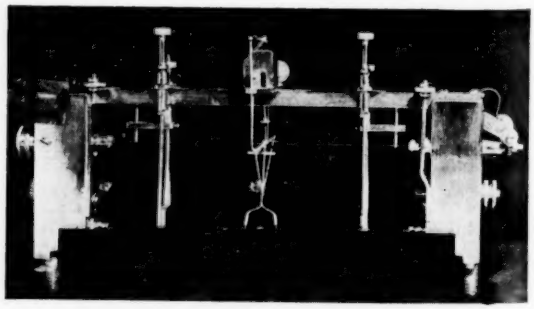

FIG. 3. Film balance.

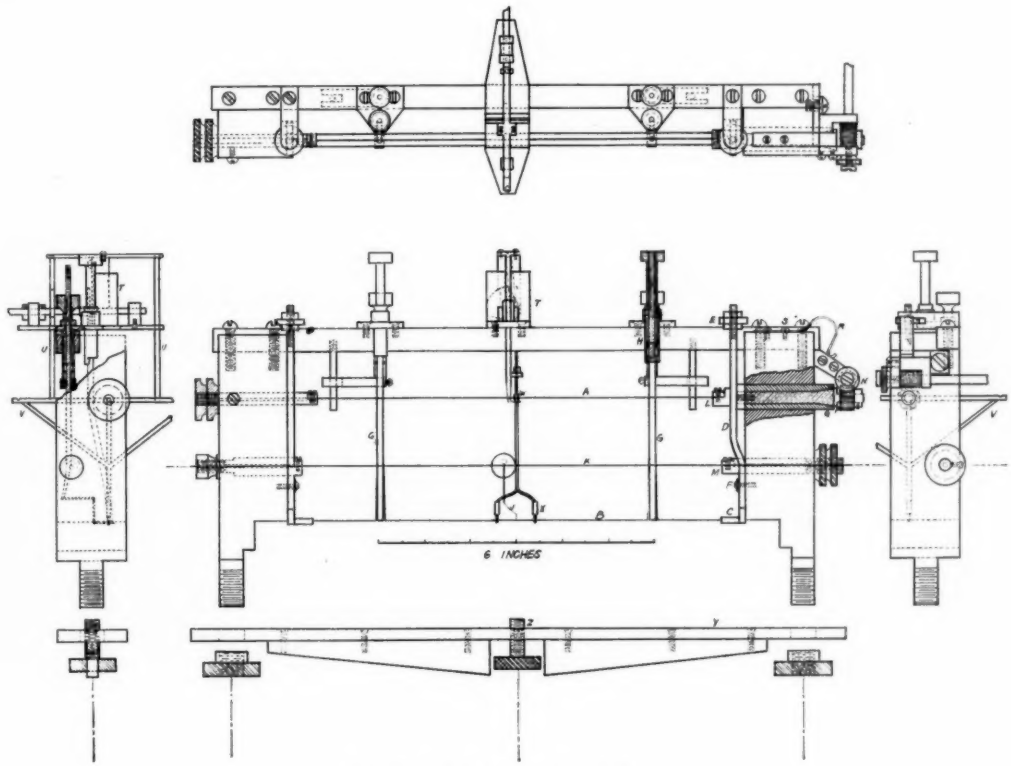

FIG. 4. Details of the film balance.

mm thick, 1.5 cm long, but are buckled to give a horizontal distance of 1 cm. They are attached to vertical strips *D*4, rather than to the posts of the torsion head. These strips *D*4 may be adjusted in a vertical direction by means of screws *E*4, to bring the float and ribbons into the same horizontal plane, in order to adjust for differences in level of the liquid in the trough. The vertical strips are clamped tightly to the posts by means of screws *F*4 to prevent leaks between the strips and the posts. This type of construction is very important in the prevention of leakage of the film past the float.

2. The gold ribbons *C*4 are attached to the float and to the vertical strips by means of Wood's metal, which obviates the use of corrosive fluxes, high temperatures and ordinary solders, all of which destroy the flexibility of the gold ribbons.

3. The float *B*4, of rolled phosphor bronze strip, is supported when not in use by two clamps, *G*4, rather than the single-acting device of Adam. The clamps operate independently. The lower half of each clamp raises the float, the upper half presses down by an enclosed spring, *H*4, and this construction does not allow the float to be raised and stored in a cramped position, as may sometimes occur if the two arms of Adam's single device are not exactly in line.

4. The small wire *J*4 which connects the float to the mirror is one mil silver wire, carefully soldered at each end.

5. The torsion wire *A*4, as well as the lower wire *K*4, both of phosphor bronze, are clamped at each end by clamps *L*4 and *M*4, the details of which are shown in the drawing. The wires pass through the clamps as shown. These screw clamps make it unnecessary to solder the phosphor bronze wires at their ends. This is important since such soldering often destroys the temper of the wires, thus causing them to lose their elasticity.

6. The torsion wire is driven by a worm-gear device *N*4, operated by a shaft leading to the exterior of the apparatus. Fractions of a degree

of arc are read on a drum and vernier on the outside shaft, which enables the pressures to be determined while the entire apparatus is enclosed and in total darkness. The wire is calibrated in terms of the outside drum, and hence any slack or irregularities in the worm-gear device are included in the calibration.

7. The end of the torsion wire next to the worm-gear is clamped to a conical piece of stainless steel *P*4 which fits into a brass sleeve *Q*4. This enables the wire to be drawn taut from the other end, and the worm-gear end of the wire is centered automatically.

8. A phosphor bronze spring *R*4 which may be adjusted by a screw *S*4 allows the worm to be fitted neatly into the worm-gear without undue friction of the gear teeth.

9. The attachment *T*4, shown more plainly in Fig. 3, *T*3, operates like the eccentric beam elevator of a balance, and is a valuable aid in both the calibration of the torsion wire and when working with the balance in the determination of film pressures. In its use, the vertical arms *U*4 may be raised to such a position that they exert a very slight vertical pull on the float, which is thus clamped into its "zero" position. In this position weights may be attached to the ends of the triangular stirrup *V*4 without a disturbance of the float and ribbons. We have found the disturbance of the float and ribbons to be very considerable without the use of this device, and this often leads to an erroneous calibration. Again, after a determination of film pressure, it is advisable to check the "zero point" of the balance, that is, the position of the float without any film on the water surface. In the earlier technique, the film was swept away, while an attempt was made to turn the wire back through its arc without a loss of equilibrium. As often happened, the float would shoot forward and exert undue torque on the wire. With the elevating device the wire can be clamped in the central position while the surface is swept several times, the drum may be turned to the zero reading, and the stirrup slowly released to check the zero-point reading. With this device we have never failed to check the zero point after adequate sweeping, whereas without the device, undue torque would disturb the float so that the zero position could not be obtained.

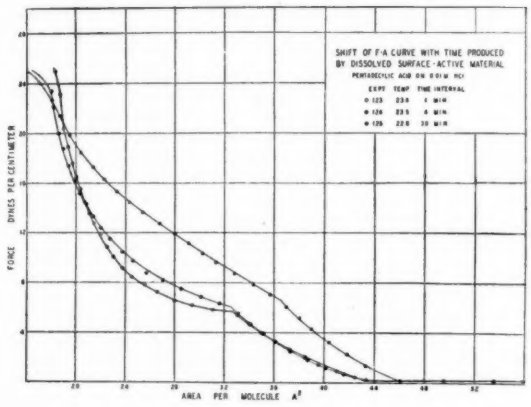
SHIFT OF F-A CURVE WITH TIME PRODUCED
BY DISSOLVED SURFACE-ACTIVE MATERIAL
PENTADECYLIC ACID ON 0·01 M HCl
EXPT TEMP TIME INTERVAL
0 123 23·0 1 MIN
● 124 23·5 6 MIN
● 125 22·0 30 MIN
FORCE DYNES PER CENTIMETER
AREA PER MOLECULE A²

FIG. 5. Effect of dissolved surface active material.

10. All parts other than the float, ribbons, stirrup and stainless steel conical shaft were made of brass, then nickel- and chromium-plated, to resist corrosion.

11. The triangular stirrup or balance beam *V*4 was produced from a sheet of Dow metal in which the open spaces were made by drilling out the metal and filing the edges. The beam was fitted with a brass ring *W*4 bolted to the beam and the phosphor bronze wire was soldered to this brass tube. Great care is necessary in soldering the wire; the heat is applied as little as possible, since the temper of the wire may be destroyed at this spot. On very acid solutions the Dow metal was attacked, due to its magnesium content, hence brass sleeves were fitted over the fingers *X*4 which pass through slots in the float. The whole beam is lightly paraffined to prevent corrosion from the acid fumes.

12. The torsion head is clamped to the trough by a bar *Y*4 which acts as a spring when the thumb screw *Z*4 is turned. This enables the torsion head to be removed directly from the trough, without injury to the paraffin surface.

4. Adjustment of Vapor Pressure

In the production of polymolecular films a mixture of a surface-active substance with an inactive oil is used. Often this oil is moderately volatile, so to reduce its evaporation, shallow troughs filled with the oil are kept inside the glass box, and a slow stream of nitrogen is bubbled through the oil to keep the pressure of the vapor more nearly that of saturation.

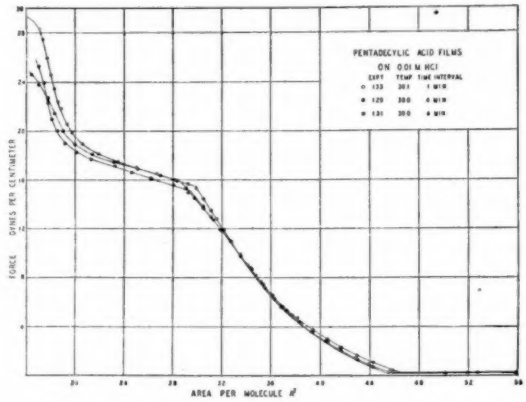

FIG. 6. Reproducibility of force-area curves.

To prevent undue evaporation of the solution in the trough during extended experiments, a second stream of nitrogen passes through a beaker of the same solution as that in the trough. This saturates the atmosphere above the film with water vapor.

5. WATER

Since the pressure of a film is a function of the hydrogen ion concentration, and because ordinary tap and distilled water often contain organic impurities, it is important to use only very pure water as the substratum for the film. The method of purification now employed in this work is that of Ellis and Kiehl.[4]

The effect of poor water is illustrated by Fig. 5. Films of pentadecylic acid on a 0.01 molar solution of hydrogen chloride in ordinary distilled water as used in the laboratory for analytical work were used. The film pressure was determined with time intervals between successive readings of 1, 4, and 30 minutes, respectively. While the film pressure is a function of the time, the wide spread between the curves in this figure is due largely to impurities in the water. With very pure water the curves with 1 and 4 minute intervals are almost identical in the region of the expanded film (Fig. 6), and a shift to lower areas with longer time intervals, is observed, as to be expected.

6. CLEANLINESS

Before each experiment the trough is freed from paraffin and cleansed by holding it very close to a jet of hot steam. The paraffin emulsifies and is carried away. The barriers are cleaned by the same procedure. The trough is then coated with paraffin while warm by painting with a solution of paraffin in a low boiling paraffin oil (ligroin) free from active materials. Care is taken not to allow the hands to touch the barriers or any part of the trough which later comes in contact with the aqueous solution with which the trough is filled.

In some laboratories more than one film is spread on the same aqueous solution. While moderately good results may be obtained in this way, our experience indicates that a higher degree of accuracy is attained if a new aqueous solution or fresh water is used for each film.

The air in the box which contains the trough and film balance should not be stirred since motion of the air brings its impurities into the surface of the liquid. In our apparatus, as already described, the moving air of the air thermostat, when this is used, is kept away from the trough and film balance by the inner box of plate glass.

7. SPREADING THE FILM

In work on equilibrium pressures monomolecular films are spread from crystals of the solid or lenses of the liquid, or the solid may be spread from its coating on a glass plate or rod.

In work upon the pressure-area relations the film is usually spread over a large molecular area by the use of a dilute solution of the film forming substance in a highly volatile paraffin oil, in benzene, or in chloroform if the substance is not soluble in the other solvents.

The high volatility of the solvent is essential for its removal from the film, but is a source of error in weighing the amounts of solution used. Obviously this particular error may be reduced by the use of a more dilute solution, so the accuracy given below refers to solutions of the concentration usually employed.

The error in weighing solutions of the ordinary concentration (order of 5 percent as given by Adam,[5]) is reduced to about 0.25 percent by the use of the weight-pipette shown in Fig. 7. The bottle consists of two necks, one for filling, one for dropping, each fitted with two caps, with

[4] S. B. Ellis and S. J. Kiehl, J. Am. Chem. Soc. **67**, 2145 (1935).

[5] N. K. Adam, *The Physics and Chemistry of Surfaces* (Clarendon Press, 1930).

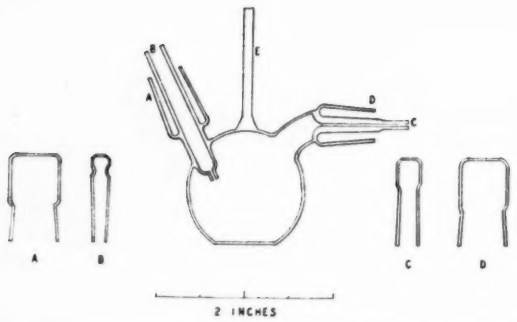

FIG. 7. Weight pipette for spreading solutions. Good tight joints on all caps. *C*-flat (drop-weight) capillary tip.

tightly fitted ground joints. The dropping tip is a fine capillary, the end of which is ground flat, according to the directions given by Harkins and Humphrey,[6] for the preparation of tips for the determination of surface tension by the drop-weight method. It is essential that this tip be as flat as possible. When properly made, the tip will prevent the solution from "climbing" around the edge of the tip-face, the drops form easily and cut off neatly as they fall.

The bottle is filled with a small funnel fitting into the left neck, the caps are placed in position and the bottle weighed, preferably with a similar bottle for a counterpoise, to five decimals, on the balance mentioned below. The cap joints must be dry during weighings. The solution is dropped on the surface by removing the two caps over the capillary tip, and tipping the bottle to allow the solution to flow into the capillary.

Slight warming with the fingers on the cloth by which the weight-pipette is held usually suffices to form four or five drops which fall slowly from the tip. When the bottle is returned to its normal position, the solution flows back into the large chamber, and leaves an almost negligible quantity on the tip-face. The caps are quickly replaced and the bottle reweighed. The bottle is handled with a clean cloth, and wiped carefully before each weighing. No correction is made for the quantity which evaporates from the tip-face, since various experiments have shown this to be of the order of 0.03–0.05 mg, while the total quantity delivered is 40–50 mg. *This precision can be attained only with a very flat tip-face.*

[6] W. D. Harkins and E. C. Humphrey, J. Am. Chem. Soc. **38**, 228 (1916).

8. ACCURACY

The screw, which measures the length of the film, may be read to 0.1 mm, or better than 0.1 percent. The graduated drum used to read the pressure on the film balance is geared 20–1 to the torsion wire, which was a high pressure wire (0.0125 inch diameter), and is never turned through more than 30°. The drum is fitted with a vernier, and is read to 0.02 dyne per centimeter although pressure differences less than 0.01 dyne per centimeter are easily detected. Resetting of the drum can be checked to within 0.04 dyne per centimeter. The temperature was controlled to less than 0.1°C but this will soon be improved to 0.005°. The precision of the area and force recording devices might be easily increased, but the error in weighing, as in all work of this character, limits the accuracy. To reduce this error, a special Ainsworth balance weighing to five decimal places was used, whereby the error in the area per molecule was reduced to about 0.25 percent. Assuming all errors to be additive, the accuracy is probably of the order of 0.5 percent.

An important feature of the apparatus, which increases the accuracy, is the moderately tight plate glass box, which incloses the trough and film balance. This decreases greatly the evaporation of the volatile constituents on the surface, and greatly reduces the contamination from vapors, liquid droplets, and dust.

Curves which illustrate the accuracy of the apparatus are exhibited in Fig. 6, which gives two determinations of the pressure-area relations at 30°. Here the time interval between successive readings is 4 minutes. A third curve, Expt. 133, gives similar values at 30.1° with time intervals of 1 minute.

With smaller torsion wires the apparatus may be made to show differences of pressure of about 0.001 dyne per cm, but the accuracy will seldom be so great.

With these improvements considerable ease and precision have resulted. The apparatus was constructed by Mr. R. Kittel, instrument maker of the Department of Chemistry, University of Chicago. Deepest thanks are due him for valuable suggestions throughout the construction of the instrument.

9. Rate of Compression

A study of the effect of the rate of compression on the character of the *F–A* curves of pentadecylic acid films was made. The results of a few experiments are shown in Fig. 8. Time intervals of one to four minutes give essentially the same force-area curve, with collapse at somewhat lower pressures associated with the slower compressions, but intervals of ten minutes or longer cause considerable shift of the curve in its upper portion, probably due to solution of the film in the substrate. An arbitrary time interval of two minutes was selected in the preliminary experiments as suitable. This allowed the film to come to equilibrium under each pressure increment, and the total time was short enough to overcome any appreciable solution of the film. As a further precaution against dissolution, the substrates were made 2 molar in sodium chloride (fused, grease-free). The sodium chloride apparently causes only a slight shift in the curve, *in toto*, to somewhat larger areas, without affecting the other characteristics. In this connection the shift with time caused by dissolved substances, shown in Fig. 5, may be mentioned again as an indication of the care to be exercised in the examination of a time effect.

10. Effect of Hydrogen Ion Concentration

The effect of the hydrogen ion concentration of the substrate upon the force-area curve of myristic acid films at 22° is shown in Fig. 9. Upon substrates which ranged from *p*H 2 to *p*H 6, practically no difference in the *F–A* curve was observed. Upon a solution of *p*H 6.5 the film is expanded at low pressures but approaches the curves given on lower *p*H's as the pressure is increased. With further increase in alkalinity to *p*H 7.3 the film becomes very expanded at low pressures, the kink disappears, and a smooth hyperbolic curve which extends to very small areas with no definite collapse point, is obtained. Upon 0.01 m NaOH, the film becomes quasi-gaseous in character, but the film contracts throughout the compression, probably due to both dissolution and collapse on this alkaline substrate. There appears to be no simple relationship between the character of the *F–A* curve and the *p*H of the substrate, other than an increased expansion on solutions of *p*H 6.5 and above. This may be attributed qualitatively to repulsion of the more highly ionized heads, but no quantitative correlation is immediately apparent. It is worthy of note that the *F–A* curve remains quite unchanged from *p*H 2 to *p*H 6, although there should be a considerable ionization of the head groups in the region *p*H 4–6.

11. Collapse Pressures

The collapse pressure of the film is largely dependent upon the rate of compression. A slow compression results in a lower collapse pressure. There seems to be no simple relationship between the collapse pressure and the hydrogen ion concentration of the substrate. However, upon slow compressions (of the order of four-minute time intervals, and longer), the second curved portion of the *F–A* curve, above the kink-point, is not observed. The films then collapse at pressures but slightly above the kink-point. This suggests that the kink may possibly be at the pressure necessary to remove the fatty acid molecule from the water surface, and may not be a phase transition or an intraphase aggregation as has been postulated by various investigators. This will be studied further.

12. Equilibrium Pressures

The equilibrium pressures of myristic acid crystals upon substrates of *p*H 2 to 8 was determined by immersing a glass rod in a melt of the acid, allowing the liquid to solidify, and

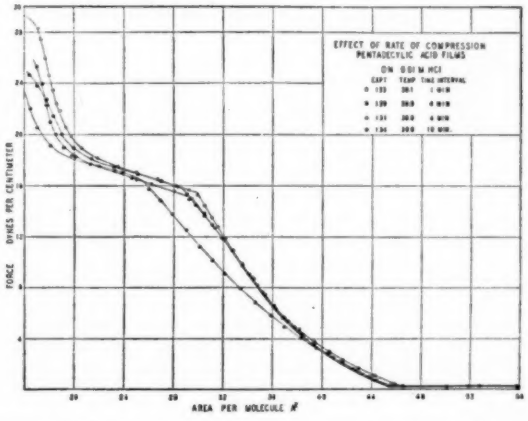

Fig. 8. Effect of time on the pressure-area relations of films of pentadecylic acid on water.

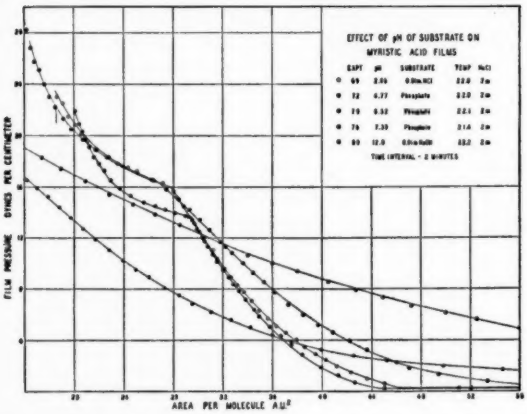

FIG. 9. Effect of hydrogen ion concentration on the pressure-area relations of films of myristic acid.

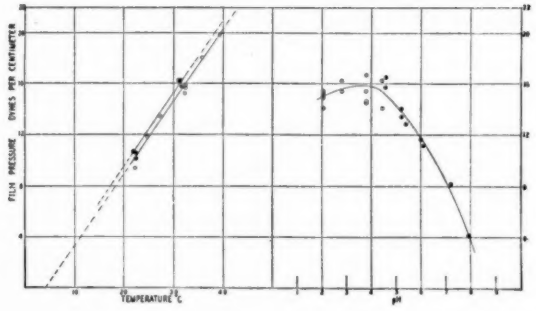

FIG. 10. Equilibrium pressure of myristic acid on water as affected by temperature and by hydrogen ion concentration. Left, equilibrium pressure of myristic acid crystals at various temperatures. Open circles, *p*H 2.05; black circles, *p*H 2.82. Right, equilibrium pressures of myristic acid crystals at 31°. Open circles, HCl; black circles, phosphate; half circles, bicarbonate.

inserting the rod into the surface of the liquid in the film trough. The film pressure built up by the crystals, after reaching a maximum, fell to lower values when alkaline solutions were employed. The results are shown in Fig. 9. The equilibrium pressures were quite constant through the range *p*H 2–4.5, then fell rapidly with further increase in alkalinity. On 0.01 m sodium hydroxide (+2 m NaCl) the equilibrium pressures rose again to 12.1 dynes, but there was no inflection point in the region *p*H 5, as might be expected if the film behaved as a fatty acid in bulk. There appears to be no relationship between the *p*H and the equilibrium pressures of the crystals which would yield information concerning the amount of ionization of the film material.

The variation of equilibrium pressure with temperature is also shown in Fig. 9. The value of dF/dT is 0.575 on *p*H 2.05, in good agreement with the value 0.568 given by Cary and Rideal.[7]

Though these results are not so striking as with proteins, they indicate a different method of attack, which should yield results of a more definite nature. A consideration of the spreading coefficient,

$$S=\gamma_1-\gamma_2-\gamma_{12}=P_{\text{collapse}},$$

where γ_1, γ_2, and γ_{12}, represent the surface tensions of the water, oil and interface respectively, indicates that the collapse pressures of liquid fatty acid films, when they collapse in a reversible manner, should be a function of the interfacial tension, which in turn has been found by several investigators to be a function of *p*H of the water phase, in an oil-water system when there are active molecules in the oil. Thus there should be some relationship between the collapse pressure of the film and the *p*H of the aqueous phase. In the above experiments this proved not to be the case, but it must be remembered that this was a solid fatty acid, and the collapse does not take place reversibly. However, with films at the interface oil-water, collapse should take place in a reversible fashion, since the fatty acid molecules can enter the oil phase with ease and then spread again when the film pressure is reduced. Ordinary oils possess too high an attraction for fatty acids to be used in this way. It will be essential that such an oil possess:

1. A relatively high interfacial tension against water.
2. A negative spreading coefficient.
3. A density greater than that of water.
4. Very slight solubility in water and hydrocarbons.

The apparatus described in this paper may be used to examine fatty acid films at such an interface, and preliminary experiments indicate that such films form with ease at the interface trichlorethane water, by spreading from a crystal on a glass rod. The trough has been modified to study such films and the work is being continued.

[7] E. Cary and E. K. Rideal, Proc. Roy. Soc. **A109**, 318 (1928).

The Role of Molecular Orientation in Photochemical Reactions in Monolayers*

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The theory of the dependence, on the molecular orientation, of the velocity of photochemical reactions in monolayers at the surface of aqueous substrates is developed. The molecular extinction coefficient in the film is discussed and a definition is given of the "apparent quantum efficiency." Consideration of the molecular thermal agitation suggests the possibility of a phase boundary potential gradient of the order of 10^8 volts per cm. Under certain conditions, the apparent quantum efficiency is proportional to the absolute temperature. Factors modifying the absorption spectrum of a compound in a monolayer are discussed. By an application of the general theory of radiation, a relation is obtained between the molecular orientation and an integral of the molecular extinction coefficient in the film over the absorption band. The molecular extinction coefficient in the film cannot be deduced *a priori* from that in solution; it is proportional to the mean value of $\sin^2\theta$ (where θ is the angle between the molecular dipole axis and the direction of the incident light) and is usually of the order of $3/2\sin^2\theta$ that in solution. The theoretical accuracy of the $\sin^2\theta$ relation is discussed and both quadrupole absorption and reabsorption of coherently scattered radiation are shown to be of no practical importance. Direct measurement of the absorption spectrum of a monolayer is essential for the absolute determination of the quantum efficiency of a photochemical reaction.

IN a number of recent investigations,[1–4] chemical reactions occurring in organic compounds spread in monolayers at the surface of aqueous substrates have been studied by observation of the phase boundary potential and surface pressure. The results of these experiments show clearly the importance and reality of the Hardy-Langmuir principle of molecular orientation in the realm of two-dimensional chemical kinetics. In photochemical processes in monolayers, a similar dependence of the reaction velocity on the orientation of the absorbing molecules has been found. (A detailed account of these experiments will be published shortly.) In the present paper, the theory of this orientational effect is given and the general processes of light absorption by monolayers are discussed in relation to the absolute measurement of the quantum efficiency of the photochemical processes occurring.

The optical anisotropy of monolayers at air-water interfaces has been demonstrated by Tronstad and Feacham[5] using the Jamin-Rayleigh method. With the aid of Strachan's development of the Drude equation,[6] they showed that, in the case of monolayers of myristic acid, the scattering index in the plane of the film is of the same order as that in bulk, while the index for the direction normal to the film is smaller by a factor of the order of 10^{-2}.

THE MOLECULAR EXTINCTION COEFFICIENT IN A MONOLAYER

It is evident that for the absorption of light by a two-dimensional monomolecular array, Beer's law in its usual form has no precise meaning. The absorbing oscillators are independent and each can capture energy from an area of incident wave-front of the order of λ^2/π (where λ is the wave-length of the incident light)[7] so that it is permissible to apply the differential analog of Beer's law, to define the molecular extinction coefficient in the film and to calculate the light absorption from a beam of given intensity. Thus the energy ΔJ absorbed by the monolayer per cm² per sec. from a normally incident beam of intensity J is given by

$$\Delta J = (2.303/6.06\times 10^{20})\epsilon n J, \qquad (1)$$

where n is the surface density specified by the number of molecules per cm², and ϵ by definition is the molecular extinction coefficient in the monolayer. The thickness of the film does not appear explicitly, but the formal analogy of Eq. (1) to Beer's law leads to a functional

* Communicated by Eric K. Rideal.
** Beit Memorial Research Fellow.
[1] Hughes and Rideal, Proc. Roy. Soc. **A140**, 253 (1933).
[2] Fosbinder and Rideal, Proc. Roy. Soc. **A143**, 61 (1933).
[3] Schulman and Rideal, Biochem. J. **27**, 1581 (1933).
[4] Gee and Rideal, Proc. Roy. Soc. **A153**, 116 (1935).
[5] Tronstad and Feacham, Proc. Roy. Soc. **A145**, 115 (1934).
[6] Strachan, Proc. Camb. Phil. Soc. **29**, 116 (1932).
[7] Rayleigh, Phil. Mag. **32**, 188 (1916).

relation, in terms of the molecular-orientation, between the molecular extinction coefficient of the compound in the film and in solution.

For examining the orientational effect, since ϵ is not known accurately, it has been found satisfactory to express the experimental data of photochemical processes by means of the "apparent quantum efficiency" ϕ_a, which is defined as the quantum efficiency calculated with the aid of Eq. (1) on the assumption that the molecular extinction coefficient in the film has the same value as that in solution in a polar solvent.

The Structure of Monolayers in Relation to Light Absorption

In liquid expanded and liquid homalic films, there is little doubt that the constituent molecules are partially sunk in the water, the polar groups being completely immersed. In liquid condensed, gelatinous and solid films, there are probably a few water molecules interspersed among the lower parts of the hydrophobic groups, but the polar groups are still surrounded by water molecules. The dielectric constant in the neighborhood of the dipoles is not known with certainty, but probably varies, usually lying between 5 and 10.

The effect of thermal agitation on the molecular orientation is a problem of great importance. At the limiting area in the liquid expanded state, the terminal dipole might be expected to be free to rotate as a result of collisions with the substrate molecules. The very low experimental value of the temperature coefficient (Fosbinder and Rideal, 1933)[2] of the vertical component of the dipole moment, as deduced from Helmholtz's equation, shows that this is not true and suggests that an orienting electric field normal to the surface must be present. An application of Langevin's theory[8] shows that an effective potential gradient of the order of 10^8 volts per cm is required in the region of the electric dipole. That a field of this order of magnitude is reasonable physically is supported by the following considerations. The total potential step at an air-water interface has not been measured directly but must be equal to the difference between the photoelectric work function for water and the contribution to the work function of the image forces. The work function for water, and solutions of electrolytes up to $N/2$ concentration, has been found by Gorlich[9] to be 6.08 volts. The order of the contribution from the image forces ϕ' can be calculated by Schottky's equation[10] $\phi' = 300e/2r_0$ volts, where r_0 is the inter-atomic distance; taking the radius of a water molecule as 1.38A, ϕ' is found to be 2.6 volts. Thus at an air-water interface there must exist a potential step of the order of 3.5 volts, which is probably due to a preferential orientation of the superficial polar water molecules. The distance over which this phase boundary potential change occurs must be of the same order as the minimum thickness of the optical transition layer, which was found by Rayleigh[11] to be 3A and by Raman and Ramdas[12] to be 5A. If a value of 4A is taken the potential gradient present is of the order of 10^8 volts per cm.

In solid and liquid condensed monolayers, the variation of orientation of the dipoles at any given area is almost certainly limited to small angular oscillations about the mean position, which is determined by the van der Waals adhesion of the hydrophobic groups in conjunction with the packing limitation set by the intermolecular repulsive fields. It will be shown below that the probability of light absorption by a molecule is proportional to $\sin^2\theta$, where θ is the angle between the molecular dipole axis and the direction of the incident light, which will be assumed throughout this paper to be normal to the surface. In monolayers of certain compounds it can be demonstrated, by means of molecular models constructed with the aid of x-ray crystallographic data, that the vertical component of the dipole moment $\bar{\mu}$, deduced from the phase boundary potential and molecular area measurements by the Helmholtz equation, is proportional to the mean value of $\cos\theta$. The important quantity for light absorption is the mean value of $\sin^2\theta$, which is less than $1-\overline{(\cos\theta)}^2$ by $(a^2/2)\sin^2\theta_0$, where θ_0 is the mean equilibrium value of θ and a the amplitude of the small

[8] Langevin, J. de physique **4**, 678 (1905).

[9] Gorlich, Ann. d. Physik **13**, 831 (1932).
[10] Schottky, Zeits. f. Physik **14**, 63 (1923).
[11] Rayleigh, *Scientific Papers* (1892), Vol. 3, p. 496.
[12] Raman and Ramdas, Phil. Mag. **3**, 220 (1927).

angular oscillation about θ_0. The amplitude a, cannot be calculated *a priori*, but if it is sufficiently small with respect to unity, no error is introduced in identifying $\overline{\sin^2\theta}$ with $1-(\overline{\cos\theta})^2$. If, however, a is not negligible, the interesting result is obtained that at $\theta_0=0$, $\overline{\sin^2\theta}=a^2/2$, so that the apparent quantum efficiency of a photochemical reaction under these conditions, which should be realized at the limiting area of certain condensed films, will be proportional to the absolute temperature. For any value of θ_0, the deviation of the observed ϕ_a from that calculated on the assumption of negligible thermal oscillation is proportional to the absolute temperature, but owing to the usual variation of with molecular area, it is only at and near the limiting area that such an effect could be detected.

General Features of the Absorption of Light by Monolayers

Accurate measurements of the absorption spectra of organic compounds spread in monolayers at an air-water interface have not yet been made, but the velocity of simple photochemical reactions shows that the molecular extinction coefficient in the film at any given wave-length is of the same order as that in solution in a polar solvent and that the absorption bands are usually not displaced by more than 100A from the position in solution. Hughes and Allsopp[13] have shown directly that magnesium naphthalocyanine gives visible green monolayers in which the molecular extinction coefficient is of the same order as in solution. Modification of the absorption spectrum in monolayers of various organic compounds adsorbed on transparent laminae of inorganic salts has been examined in considerable detail by de Boer[14] but the results are not capable of direct extension to monolayers on aqueous substrates.

In relation to the absorption of light, the general physical conditions in a monolayer at a water surface are closely analogous to those present in solution in a polar solvent. The collision damping is of similar importance, producing a Lorentz wave-length half-breadth $\Delta\lambda$[15] for the collision broadened line of wave-length λ, of the order of $\Delta\lambda=\lambda^2Z/c\pi$. Z, the collision frequency between a film molecule and the substrate molecules, can be obtained from the approximate equation $Z=3\pi\eta\sigma/2m$ where σ and m are the diameter and mass of the film molecule and η is the viscosity of the solvent. For molecules such as stearic acid on water, Z is of the order of 10^{13} per second, so that at $\lambda=2400$A $\Delta\lambda=10$A. The collision displacement of a line is of the order of $\Delta\lambda/2$[16] and is thus negligible with respect to that produced by the inhomogeneous Stark effect of the electric fields of the colliding substrate molecules. According to the theory of Stern[17] the fields of water molecules can, during collisions, produce wave-length displacements of the absorption spectrum of the order of 100–1000A, such as were found for mercury atoms in solution by Reichardt and Bonhoeffer.[18]

It is possible that there is a not inconsiderable modification of the absorption spectrum in a monolayer due to the homogeneous Stark effect produced by the orienting field at the phase boundary. Analogy with the linear Stark effect for a diatomic molecule with a permanent electric dipole suggests that the order of the wave-length displacement $\Delta\lambda$ of an absorption line of wave-length λ is given by $\Delta\lambda=(\lambda^2/hc)p\cdot E$, where p is the molecular dipole moment and E the applied electric field. A phase boundary potential gradient of the order of 10^8 volts per cm may produce a shift of the ultraviolet absorption spectrum of the order of 100A, and accurate measurement of the absorption spectrum of a monolayer may provide evidence for the existence and magnitude of the orienting field.

It is now necessary to consider briefly the transition probability which determines the absorption intensity, in the presence of the inhomogeneous, and possibly also the homogeneous, electric fields. The molecules dealt with experimentally are extremely complex, so that even in the simplest cases, an exact treatment of the Stark effect is quite impossible. Analogy

[13] Hughes and Allsopp, Nature **137**, 503 (1936).
[14] de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge, 1935), Chap. 8.
[15] Lorentz, Proc. Amst. Acad. **18**, 134 (1915).
[16] Lenz, Zeits. f. Physik **80**, 423 (1933).
[17] Stern, Physik. Zeits. **23**, 476 (1922).
[18] Reichardt and Bonhoeffer, Zeits. f. Physik **67**, 780 (1931).

with diatomic molecules possessing a permanent electric moment[19] suggests that under certain, probably very restricted, conditions the summation rule may still hold, so that the oscillator strength corresponding to a given transition is invariant. Although the field strengths are very great, and the electron transition is at the periphery of the atom, the validity of the summation rule has been confirmed by Reichardt[20] for the 2537A absorption line of mercury, modified by solution in hexane.

Light Absorption and Molecular Orientation

We must first consider a simplified model in which the thermal agitation of the molecules is absent and the perturbing fields, apart from the incident light, are small. The monolayer consists of a two-dimensional array of molecules represented by electric dipoles whose axes are inclined at a constant angle θ to the normal to the surface. The azimuthal orientation is random. No details of the molecular distribution are specified but macroscopic uniformity is necessary. The incident light is normal to the surface; it is unpolarized and has a continuous spectral distribution with $N(\nu)$ quanta per cm^2 per second per unit frequency range at ν, so that the intensity J_ν per unit frequency range at ν is $J_\nu = N(\nu)h\nu$. n is the total number of molecules per cm^2. The molecular resonance frequencies do not coincide on account of the perturbing fields and $n_\nu d\nu$ is the molecular surface density of molecules with proper frequencies between ν and $\nu+d\nu$. ϵ_ν is the molecular extinction coefficient in the film at the frequency ν. Thus two spectral distributions have to be considered:

1. That of the incident light; in which J_ν varies very slowly with frequency.

2. That of the proper frequencies of the absorbing oscillators. ϵ_ν varies rapidly with frequency over the absorption band and has only non-zero values over a narrow range.

The probability P_ν of absorption by a molecule with a permanent electric dipole moment of a quantum per second from an incident beam of $N(\nu)$ quanta per cm^2 per second per unit frequency range at frequency ν is proportional to $|(p\cdot E)|^2$, the square of the modulus of the scalar product of the electric moment p and the electric vector E of the incident light beam.

When the beam is plane polarized with the electric vector parallel to the x axis and the molecular dipole axis is also in the direction of the x axis, P_ν is given, to a first approximation, by

$$P_\nu = (8\pi^3 e^2/hc)\,|x_{ik}|^2 N(\nu)\nu, \tag{2}$$

where i, k signify the upper and lower molecular energy levels involved and x_{ik} is the corresponding matrix element of the x coordinate:

$$x_{ik} = \int \psi_i^*\Big(\sum_n x_n\Big)\psi_k dx_1 \cdots dx_n dy_1 \cdots dy_n dz_1 \cdots dz_n, \tag{3}$$

where $x_l y_l z_l$ are the coordinates of the lth particle and the summation is extended over the n particles (electrons and nuclei) in the molecule. This result can be obtained by two methods by means of Dirac's perturbation theory[21] and contains an integration over the whole spectrum of the incident light.

Thus the number of quanta absorbed per cm^2 of the model film per second in the frequency range ν, $\nu+d\nu$ from an incident unpolarized beam of $N(\nu)$ quanta per cm^2 per second per unit frequency range at frequency ν, is, averaging over all directions of polarization of the incident beam and of azimuthal orientation of the molecules, given by

$$P_\nu n_\nu d\nu = \frac{8\pi^3 e^2}{hc}|r_{ik}|^2 \frac{\sin^2\theta}{2} N(\nu)\nu n_\nu d\nu, \tag{4}$$

where r_{ik} is the matrix element of the coordinate vector r, whose components are x, y, z.

In terms of the molecular extinction coefficient in the film, Eq. (1) shows that

$$P_\nu n_\nu d\nu = \frac{2.303}{6.06\times 10^{20}} n_\nu d\nu \int_0^\infty \frac{\epsilon_\nu J_\nu d\nu}{h\nu}. \tag{5}$$

J_ν varies very slowly with frequency so that

$$P_\nu n_\nu d\nu = \frac{2.303}{6.06\times 10^{20}} n_\nu d\nu N(\nu)\nu \int \frac{\epsilon_\nu d\nu}{\nu}, \tag{6}$$

where the frequency range of integration is now

[19] Kronig, *Band Spectra and Molecular Structure* (Cambridge, 1930), p. 99.

[20] Reichardt, Zeits. f. Physik **70**, 516 (1931).

[21] Dirac, *Principles of Quantum Mechanics* (Oxford, 1930), Chaps. 9, 12.

extended over the absorption band. Hence from Eqs. (4) and (6)

$$\frac{8\pi^3 e^2}{hc}|r_{ik}|^2\frac{\sin^2\theta}{2}=\frac{2.303}{6.06\times10^{20}}\int\frac{\epsilon_\nu d\nu}{\nu}. \quad (7)$$

This equation is analogous to the well-known relation[22–25] between the Einstein B coefficient and the integral of the absorption coefficient of a line:

$$B_{ki}=c/N_k\int(\alpha' d\nu/h\nu), \quad (8)$$

where B_{ki} is Einstein's absorption probability coefficient defined in terms of the radiation density, N_k is the number of absorbing molecules per cm³ in the lower state k and α' is the "natural extinction coefficient." Introduction of the usual expression for B_{ki} shows more clearly the relation between Eqs. (7) and (8):

$$\frac{g_i 8\pi^3 e^2}{g_k 3hc}|r_{ik}|^2=\frac{2.303}{6.06\times10^{20}}\int\frac{\epsilon_\nu' d\nu}{\nu}, \quad (9)$$

where ϵ_ν' is the molecular extinction coefficient in bulk. The statistical weights of the upper and lower states g_i and g_k, are usually unity.

Eqs. (7) and (9) are deduced assuming the presence of weak or negligible perturbing fields, and the formal difference between them is due to the averaging over all values of $\sin^2\theta$ in Eq. (9). When strong perturbing fields are introduced, so that Eq. (7) corresponds to a real monolayer and Eq. (9) to a solution, $|r_{ik}|^2$ in each case is replaced by a sum $\sum_{i'k'}|r_{i'k'}|^2$ and the absorption integrals may change, but if the summation rule is valid, these quantities are invariant; there is however no *a priori* demonstration that in any given case this is true.

Eq. (7) shows the relation between the molecular extinction coefficient in the film and the molecular orientation. As discussed above, $\sin^2\theta$ must be averaged over those values of θ allowed by the thermal agitation and orientational oscillation at any given molecular area. Thus the fundamental result capable of experimental test is that the molecular extinction coefficient in the film is proportional to $\overline{\sin^2\theta}$. Comparison of Eqs. (7) and (9) demonstrates that no exact relation exists between ϵ_ν' the molecular extinction coefficient in solution and ϵ_ν, that in the film. In general,

$$\epsilon_\nu=3/2f(\nu)\,\overline{\sin^2\theta}, \quad (10)$$

where $f(\nu)$ is an extremely complicated function of ν, which cannot be calculated theoretically in terms of ϵ_ν', but which usually is of the same order as ϵ_ν'. From these considerations it is evident that direct measurement of the absorption spectrum of a monolayer is essential for the absolute determination of the quantum efficiency of a photochemical process occurring in the monolayer.

Accuracy of the $\sin^2\theta$ Relation

There are three factors which one may envisage as capable of causing departures from the $\sin^2\theta$ relation, namely:

1. Inaccuracy of Eq. (2) due to neglect of significant terms of higher order of approximation.
2. Reabsorption of light coherently scattered in the monolayer.
3. Quadrupole absorption.

Each of these will be considered briefly and shown to be of no importance under experimental conditions.

Eq. (2) is obtained by the perturbation theory as a second-order term. The higher order approximations can be easily calculated and it is found that, while the third-order term vanishes, the fourth-order term does not and leads to the following modification of Eq. (2):

$$P_\nu=8\pi^3/hc\,|(\alpha'|p|\alpha'')|^2N(\nu)\nu - \frac{16\pi^6N(\nu)^2\nu^2}{h^2c^2}\sum_{\alpha'''}|(\alpha'|p|\alpha'')|^2|(\alpha''|p|\alpha''')|^2, \quad (11)$$

where $\nu=\nu(\alpha'\alpha'')$ the frequency of the absorbed radiation being connected with states α', α'' and the summation in the second term is over all other states α'''. Under the conditions in photochemical experiments, an incident beam with $N(\nu)$ of the order of one quantum per cm² per second per unit frequency range in the wavelength band 2350–2400A is employed, so that the first term in Eq. (11) is of the order of

[22] Becker, Zeits. f. Physik **18**, 325 (1923).
[23] Tolman, Phys. Rev. **23**, 693 (1924).
[24] Milne. Mon. Not. Roy. Astronom. Soc. **85**, 117 (1924).
[25] Joos, *Handbuch der Experimental Physik* (Leipzig, 1927), Vol. 21, p. 102.

1.10^{-3}, while the second term is of the order of 5.10^{-7} and hence is negligible.

The process of equating the expressions on the right sides of Eqs. (4) and (6) neglects the negative absorption, and is equivalent to omitting from the left side of Eq. (7) a factor $(1-g_iN_i/g_kN_k)$. Under experimental conditions, light absorption is the only important mechanism responsible for the formation of excited molecules, so that the proportion of excited molecules in the film N_i/N_k is of the order of 10^{-12}.

The coherent scattering in the film can be calculated by regarding the molecules as Hertzian oscillators. With an unpolarized normally incident beam of intensity J_{inc}, the order of the intensity $J_{r\theta}$ scattered by a molecule at a distance r of the order of the molecular radius a in a direction making an angle θ with the normal is, on the assumption that the molecular polarizability is of the order of a^3, given by the expression

$$J_{r\theta}/J_{\text{inc}}=(a^6/r^4)(2\pi/\lambda)^2((1+\cos^2\theta)/2). \quad (12)$$

Only the immediately adjacent molecules can have an appreciable effect, and even at $r=2a$, for $\lambda=2400$A, $J_{r\theta}/J_{\text{inc}}$ is of the order of 10^{-6}. For large r, $J_{r\theta}/J_{\text{inc}}$ is of the order of $a^6/r^2\lambda^4$ which cannot be greater than 10^{-18}. Thus it is certain that coherent scattering can never be of importance in photochemical processes in monolayers.

It is not evident *a priori* that a film molecule can be adequately represented by an electric dipole and absorption by an electric quadrupole molecule will now be considered.[26] The Einstein probability coefficient B_{ki}, for absorption of radiation of frequency ν_{ik} by a quadrupole is easily found to be

$$B_{ki}=(g_i/g_k)(4/5)(\pi^5\nu_{ik}^2/c^2h^2)\,|Q_{ik}|^2 \quad (13)$$

in the usual notation, where Q_{ik}, the matrix component of the quadrupole moment is defined by

$$Q_{ik}=-e\int\psi_i^*(\sum_n r_n^2)\psi_k dx_1\cdots dx_n dy_1 \cdots dy_n dz_1\cdots dz_n. \quad (14)$$

By induction from Eqs. (7) and (8), it can be seen that the molecular extinction coefficient in a film of quadrupoles is of the order of $15\,\overline{\sin^4\theta}/8$ that in solution, where θ is the angle between the quadrupole axis and the direction of the incident beam. However, for $\lambda=2400$A and $r=3$A, B_{ki} (quadrupole)/B_{ki} (dipole) is of the order of 10^{-5}, so that no photochemical reaction due to quadrupole absorption could possibly be detected.

I wish to thank Professor E. K. Rideal for his stimulating criticism and continued help throughout this investigation.

[26] Rubinowicz, Physik. Zeits. **19**, 440 (1918).

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The Evaluation of Molecular Dipole Moments from the Data of Electrical Stern-Gerlach Experiments

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RODEBUSH, Murray, and Bixler[1] report measurements of the electrical dipole moments of the alkali halides by the molecular beam method, which gave values for KCl and KI much greater than those obtained by Scheffers,[2] also by a beam method. Scheffers used a wire and concentric cylinder to obtain the necessary inhomogeneous electric field, whereas Rodebush Murray, and Bixler used the Rabi type of field (parallel plate condenser), and they suggest that

[1] W. H. Rodebush, L. A. Murray, and M. E. Bixler, J. Chem. Phys. **4**, 372 (1936). See also W. H. Rodebush, ibid. p. 536.

[2] H. Scheffers, Physik. Zeits. **35**, 425 (1934).

one cause of the discrepancy between their values and those of Scheffers might lie in a possible error in Fraser's calculation[3] of the effective mean square $(E^2)_{av}$ of the electric field in terms of the field E_c between the plates of the condenser. We have therefore reviewed the calculations on which Fraser's quoted value $(E^2)_{av}=k\cdot E_c^2$, $k=0.6$ is based, with the following results.

1. The value $k=0.6$, obtained by a process of quadrature, is a particular value, appropriate to the geometry used by Estermann and Fraser,[4] and is not generally applicable. Unfortunately this is by no means clear from Fraser's text.

2. The effective mean square $(E^2)_{av}$ is determined by evaluating the integral

$$\frac{1}{l}\int_0^l E^2\cdot dl,$$

where l is the distance between the image slit ($E_0=0$) and the detector slit. Thus the value of $(E^2)_{av}$ depends on the geometry of the apparatus, and it is more convenient to have a general expression for $(E^2)_{av}/E_c^2$, soluble directly on insertion of the numerical values appropriate to a given experiment, than to use as hitherto graphical methods of evaluation. Such an expression has been obtained by one of us (J. V. H.), as follows.

Let the x axis be identified with the edge of the condenser, considered infinitely extended in that direction; let $2h$ (z direction) be the width of the gap; and let the positive direction of y lie within the condenser. Then, if y_1, y_2 are the y coordinates of image slit and detector slit, respectively, the above integral is identical with

$$\frac{1}{y_2-y_1}\cdot\int_{y_1}^{y_2} E^2\cdot dy.$$

Now E and y can both be expressed as functions of a single parameter[5] U; and we may write

$$(E^2)_{av}=\frac{\int_{U_1}^{U_2} E^2\cdot\frac{dy}{dU}\cdot dU}{\int_{U_1}^{U_2}\frac{dy}{dU}\cdot dU},$$

whence

$$\frac{(E^2)_{av}}{E_c^2}=\frac{U_1-U_2-\log(e^{U_1}+1)+\log(e^{U_2}+1)}{U_1-U_2+e^{U_1}-e^{U_2}},$$

where U_1, U_2 are obtained from y_1, y_2 by numerical solution of the equation

$$(y/h)\cdot\pi+1=-(e^U+U).$$

3. These formulae, applied to the experimental arrangement of Rodebush, Murray, and Bixler, give $k=0.85$. Now $\mu:1/k^{\frac{1}{2}}$, hence their values are to be multiplied by the factor $(0.6/0.85)^{\frac{1}{2}}=0.84$. Thus μ(KCl) becomes, in Debye units, 8.00, μ(KI) becomes 9.24, as compared with the corresponding values 6.3 and 6.8, respectively, obtained by Scheffers.

4. The two sets of results still differ considerably, but Professor Rodebush is of the opinion that the discrepancy between his values as here revised and those of Scheffers is covered by a probable experimental error.[6] Nevertheless it may possibly be significant that Estermann and Fraser obtained a high value for μ(HCl) using essentially the same method. Errors, arising from an application of Rabi's formulae in cases where the angle between the incident beam and the field plates is small, lead, however, rather to too small values of the moment;[7] although it should be observed that Wohlwill's low value for the moment of paranitraniline is irrelevant,[8] since he evaluated his results by applying the theory of the linear rotator to a polyatomic molecule. A careful reexamination of the theory of the Rabi field has not revealed any unsuspected source of error.

[3] R. G. J. Fraser, *Molecular Rays* (Cambridge, 1931), p. 171.
[4] I. Estermann and R. G. J. Fraser, J. Chem. Phys. **1**, 390 (1933).
[5] Cf. Jeans, *Electricity and Magnetism*, fifth edition, (Cambridge, 1927), p. 271.
[6] Private communication.
[7] H. Scheffers, Physik. Zeits. **34**, 245 (1933).
[8] Cf. H. Scheffers, Physik. Zeits. **35**, 425 (1934).

Theoretical Considerations Concerning the Reactions Between Ethylene and the Halogens and Their Products

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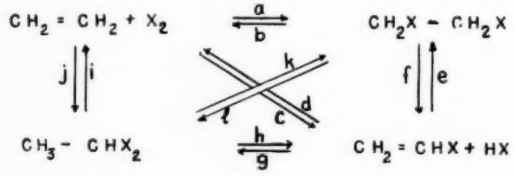
Ethylene may react with a halogen by a substitution reaction to give a vinyl halide and hydrogen halide, or the halogen may add to the double bond to give 1,2-dihalo-ethane or rearrange and give ethylidene halide. It is found that the symmetrical addition is favored in the case of each halogen. 1,2-dihalo-ethane, or the corresponding ethylidene compound may decompose to give ethylene and the halogen, or the vinyl halide and hydrogen halide. It is found that ethylene formation is favored in the bromine and iodine derivatives, whereas, in agreement with experiment, vinyl chloride and HCl would be produced from either 1,2-dichlor-ethane or ethylidene chloride. In most of the reactions considered mechanisms involving free radicals are slightly more probable than the corresponding unimolecular or bimolecular reactions.

INTRODUCTION

A CONVENIENT and useful scheme for representing the various possible reactions between ethylene and the halogens is as follows:



X denotes any one of the halogens Cl, Br, or I. The twelve reactions given in the above scheme are labeled a, b, c, $\cdots$ l. In this paper we shall calculate, theoretically, the activation energies of the various reactions and then predict the behavior of the different compounds given in the scheme. From each corner of the above rectangle arrows go out in three directions, and which of the three courses is taken will depend upon the rate or activation energy of the reaction concerned.

Sherman and Sun[1] were primarily interested in the addition of the halogens to ethylene, and the decomposition of the products formed—i.e., reactions a and b—and calculated the relevant activation energies by the so-called semi-empirical method of Eyring. We shall incorporate their results in the present paper and extend the calculations to other reactions, using the same method.

Sun[2] has calculated the activation energies involved in the addition of the hydrogen halides to a double bond by Eyring's method, but we have repeated his work because he did not use Morse constants consistent with our choice of values. Our results differ only slightly from his.

CALCULATIONS

The method of calculating activation energies by the semi-empirical method of Eyring has frequently been described elsewhere,[3] and will not be repeated here. We shall merely give in Table I the constants used for constructing the various Morse curves in question.

The constants used for the bonds C−C, C−Cl, C−Br, C−I, Cl_2, Br_2, and I_2 are as given in Table I of the paper of Sherman and Sun. (See reference 1.)

RESULTS

The activation energies and heats of reaction, calculated from our Morse constants, are given in Table II.

Based on considerable experience it should be pointed out that the calculated values of activation energies are not very sensitive to the particular bond constants chosen. For example, in the reaction $C_2H_4+H_2\rightarrow C_2H_6$ increasing the strength of the H−H bond by 5 kcal. increases A by less than 2 kcal. This is particularly true for the difference between two calculated activation energies and since almost all our reasoning is based upon a knowledge of such differences it is highly probable that none of our conclusions

[1] Sherman and Sun, J. Am. Chem. Soc. **56**, 1096 (1934).
[2] Sun, J. Chinese Chem. Soc. **41**, 98 (1936).
[3] See, for example, Van Vleck and Sherman, Rev. Mod. Phys. **7**, 167 (1935).

TABLE I.

Bond	r_0(A)	ω_0 (cm^{-1})	D (kcal.)
H−Cl	1.28[a]	2841	101.0[b]
H−Br	1.42[a]	2603	86.2[b]
H−I	1.62[a]	2233[c]	70.8[b]
C−H	1.12[d]	2930[d]	99.6[e]

[a] Weizel, *Bandenspektrum* (Leipzig, 1931).
[b] Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).
[c] Kohlrausch, *Der Smekal-Raman Effekt* (J. Springer, Berlin, 1931).
[d] Mulliken, Rev. Mod. Phys. **4**, 1 (1932).
[e] Pauling and J. Sherman, J. Chem. Phys. **1**, 606 (1933).

would be changed by slightly altering our Morse constants.

In Table II the A's are activation energies, ordinarily defined by the Arrhenius equation $d\ln k/dT = A/RT^2$.[4] ΔH is the change in heat content of the reaction, calculated by taking the difference between the strengths of the bonds formed and broken. A minus sign means that the reaction, as read from left to right, is exothermic.

The activation energies of the various reactions in the scheme given in the introduction may now be determined. These will, of course, depend upon the particular mechanism assumed. We proceed as follows:

TABLE II.

Reaction	Halogen	A	A'	ΔH
1. $CH_2=CH_2+X_2 \underset{A_1'}{\overset{A_1}{\rightleftarrows}} CH_2X-CH_2X$	Cl	25.2	80.4	−55.2
	Br	24.4	50.2	−25.8
	I	22.4	30.0	− 7.6
2. $CH_2=CH_2+X_2 \underset{A_2'}{\overset{A_2}{\rightleftarrows}} CH_2=CHX+HX$	Cl	45.0	68.0	−23.0
	Br	47.0	46.4	+ 0.6
	I	54.0	33.8	+20.2
3. $CH_2=CHX+HX \underset{A_3'}{\overset{A_3}{\rightleftarrows}} CH_2X-CH_2X$	Cl	43.5	75.7	−32.2
	Br	41.9	68.3	−26.4
	I	36.4	64.2	−27.8
4. $CH_2=CH_2+X \underset{A_4'}{\overset{A_4}{\rightleftarrows}} CH_2-CH_2X$	Cl	0	33.6	−33.6
	Br	0	13.0	−13.0
	I	2.2	1.2	+ 1.0
5. $CH_2-CH_2X+X_2 \underset{A_5'}{\overset{A_5}{\rightleftarrows}} CH_2X-CH_2X+X$	Cl	3.0	24.6	−21.6
	Br	2.3	15.1	−12.8
	I	1.8	10.4	− 8.6
6. $CH_2=CH_2+X \underset{A_6'}{\overset{A_6}{\rightleftarrows}} CH=CH_2+HX$	Cl	14.9	16.3	− 1.4
	Br	23.4	10.0	+13.4
	I	33.5	4.7	+28.8
7. $CH=CH_2+X_2 \underset{A_7'}{\overset{A_7}{\rightleftarrows}} CH_2=CHX+X$	Cl	3.0	24.6	−21.6
	Br	2.3	15.1	−12.8
	I	1.8	10.4	− 8.6
8. $CH_2X-CHX+HX \underset{A_8'}{\overset{A_8}{\rightleftarrows}} CH_2X-CH_2X+X$	Cl	16.3	14.9	+ 1.4
	Br	10.0	23.4	−13.4
	I	4.7	33.5	−28.8

[4] For a more exact definition see Eyring, J. Chem. Phys. **3**, 107 (1934).

Reaction a: $CH_2=CH_2+X_2 \rightarrow CH_2X-CH_2X.$

If the mechanism of this reaction is considered to be bimolecular the activation energies are as given in Table II for reaction 1. The reaction may, however, proceed by the following chain mechanism for chlorine and bromine:

$$X_2 \rightleftarrows 2X, \tag{1}$$

$$X+CH_2=CH_2 \rightarrow CH_2-CH_2X, \tag{2}$$

$$CH_2-CH_2X+X_2 \rightarrow CH_2X-CH_2X+X; \text{ etc.} \tag{3}$$

The above reactions constitute a chain since the halogen atom which is used up in (2) is formed in reaction (3), and so may react with another ethylene molecule, etc.

By the usual methods it may be shown that for this mechanism the over-all activation energy of reaction a is equal to the activation energy of reaction (2) plus one-half the heat of dissociation of the halogen, i.e., $A = A_{(2)} + \frac{1}{2}D_{X_2}$.[5] This equals $0+28.5=28.5$ kcal. for chlorine and $0+22.6=22.6$ kcal. for bromine.

[5] We shall illustrate the method by deriving the given relation in this particular case. Let the k's be the specific reaction rate constants of the reactions concerned, and let E denote $CH_2=CH_2$; EX, CH_2-CH_2X; and K the equilibrium constant of reaction (1). Then, assuming that the rate of a reaction is proportional to the concentration of reacting substances, and the concentration of the free radicals do not change after the initial instant, we have

$$-\frac{d(E)}{dt} = k_2(X)(E);$$

$$-\frac{d(X_2)}{dt} = k_1(X_2) - k_1'(X)^2 + k_3(X_2)(EX),$$

$$\frac{d(X)}{dt} = 2k_1(X_2) - k_1'(X)^2 - k_2(X)(E) + k_3(X_2)(EX) = 0,$$

$$\frac{d(EX)}{dt} = k_2(X)(E) - k_3(X_2)(EX) = 0.$$

Therefore $2k_1(X_2) = k_1'(X)^2$, or

$$(X) = \sqrt{\frac{2k_1}{k_1'}}(X_2)^{\frac{1}{2}} = \sqrt{2}K^{\frac{1}{2}}(X_2)^{\frac{1}{2}},$$

$$(EX) = \frac{k_2}{k_3}\sqrt{\frac{2k_1}{k_1'}}\frac{(X_2)^{\frac{1}{2}}}{(X_2)}(E),$$

$$-\frac{d(E)}{dt} = -\frac{d(X_2)}{dt} = \sqrt{2}k_2K^{\frac{1}{2}}(X_2)^{\frac{1}{2}}(E).$$

But, neglecting entropy, and remembering $k = \text{constant} \cdot e^{-A/RT}$, $\text{constant} \cdot e^{-A/RT} = \text{constant} \cdot e^{-A_{(2)}/RT} \cdot e^{-\Delta H/2RT} = \text{const} \cdot e^{-A_{(2)}+\frac{1}{2}\Delta H/RT}$ or $A = A_{(2)} + \frac{1}{2}D_{X_2}$.

For iodine it is clear from Table II that the chain mechanism just given must be modified by including the reverse of reaction (2), since the activation energies of the forward and reverse reaction only differ by one kilogram calorie. We then have $A=A_{(2)}+A_{(3)}+\frac{1}{2}D_{I_2}-A'_{(2)}$, where $A'_{(2)}$ stands for the activation energy of the reaction which is the reverse of (2). Hence, $A=2.2+1.8+17.7-1.2=20.5$ kcal.

Reaction b: $CH_2X-CH_2X\rightarrow CH_2=CH_2+X_2$.

This reaction may occur as a unimolecular decomposition, in which case the activation energies are as given in Table II for reaction 1 (the A''s).

In the case of the bromine and iodine compounds the following chain mechanism is possible:

$$CH_2X-CH_2X\rightleftarrows\underset{|}{C}H_2-CH_2X+X \quad (1)$$

$$X+CH_2X-CH_2X\rightarrow\underset{|}{C}H_2-CH_2X+X_2, \quad (2)$$

$$\underset{|}{C}H_2-CH_2X\rightarrow CH_2=CH_2+X. \quad (3)$$

The activation energy of the decomposition reaction then becomes $A=\frac{1}{2}(D_{C-X}+A_{(2)}+A_{(3)})$. This is $\frac{1}{2}(58.0+15.1+13.0)=43.1$ kcal. for the bromine derivative and $\frac{1}{2}(44+10.4+1.2)=27.8$ kcal. for the iodine compound.

In the case of CH_2Cl-CH_2Cl the above mechanism does not appear reasonable because the reaction $\underset{|}{C}H_2-CH_2Cl\rightarrow CH_2=CH_2+Cl$ is endothermic 33.6 kcal., i.e., the decomposition of $\underset{|}{C}H_2-CH_2Cl$ is improbable compared to its reaction, since the activation energy of a reaction involving a free radical (provided the reaction is not endothermic) is much less than this. The following scheme is suggested:

$$CH_2Cl-CH_2Cl\rightarrow\underset{|}{C}H_2-CH_2Cl+Cl, \quad (1)$$

$$Cl+CH_2Cl-CH_2Cl\rightarrow\underset{|}{C}H_2-CH_2Cl+Cl_2, \quad (2)$$

$$Cl+\underset{|}{C}H_2-CH_2Cl\rightarrow CH_2=CH_2+Cl_2.^{6} \quad (3)$$

It is seen that the above reactions do not constitute a chain but rather a series of reactions in which the first one is taken to be the slow step, i.e., is rate determining. Although (3) involves two free radicals, the concentrations of which are small, its rate is considered to be greater than that of reaction (1) because of the approximately zero value for the activation energy of this reaction and the large value for (1). The activation energy for the decomposition of CH_2Cl-CH_2Cl thus becomes equal to that of the first reaction,—assumed to equal or exceed its endothermicity. Hence $A=D_{C-Cl}=78.6$ kcal.

Reaction *b* is really auto-catalytic since X_2, a product of the reaction, may act as a catalyst for the decomposition of the dihalide. The following mechanism is suggested in the case of the bromine and iodine derivatives:

$$X_2\rightleftarrows 2X, \quad (1)$$

$$X+CH_2X-CH_2X\rightarrow\underset{|}{C}H_2-CH_2X+X_2, \quad (2)$$

$$\underset{|}{C}H_2-CH_2X\rightarrow CH_2=CH_2+X. \quad (3)$$

In this case $A=A_{(2)}+\frac{1}{2}D_{X_2}=15.1+22.6=37.7$ kcal. for the bromine compound[7] and $10.4+17.7=28.1$ kcal. for the iodine derivative.

For the dichloride the following mechanism is considered:

$$Cl_2\rightleftarrows 2Cl, \quad (1)$$

$$Cl+CH_2Cl-CH_2Cl\rightarrow\underset{|}{C}H_2-CH_2Cl+Cl_2, \quad (2)$$

$$Cl+\underset{|}{C}H_2-CH_2Cl\rightarrow CH_2=CH_2+Cl_2. \quad (3)$$

Here the dissociation of Cl_2 is the slow step and hence $A=D_{Cl_2}=57.0$ kcal.[8]

Reaction c: $CH_2=CH_2+X_2\rightarrow CH_2=CHX+HX$.

If this reaction has a bimolecular mechanism as written the activation energies are as given in Table II. The following chain mechanism is however possible:

$$X_2\rightleftarrows 2X, \quad (1)$$

$$X+CH_2=CH_2\rightarrow\underset{|}{C}H=CH_2+HX, \quad (2)$$

$$\underset{|}{C}H=CH_2+X_2\rightarrow CHX=CH_2+X, \text{ etc.} \quad (3)$$

[6] It is of course more probable that the monochlorethylene free radical collide with the dichlor derivative than a chlorine atom, but the most likely chemical reaction would not be detectable in this case, i.e., $CH_2Cl-CH_2Cl+\underset{|}{C}H_2-CH_2Cl\rightarrow CH_2Cl-\underset{|}{C}H_2+CH_2Cl-CH_2Cl$.

[7] This value differs from the value given in reference 1 because in that paper ΔH_7 of Table II was incorrectly calculated.

[8] This value differs from that given in reference 1 because there the same mechanism was assumed for the decomposition of the dichloride as for the other dihalide derivatives.

The over-all activation energy is $A = A_{(2)} + \frac{1}{2}D_{X_2}$. For the chlorine, bromine, and iodine compound the reverse of reaction (2) should be considered but this does not affect the value of A since this reverse reaction is slow compared to reaction (3). Hence $A = 14.9 + 28.5 = 43.4$ kcal. for chlorine, $23.4 + 22.6 = 46.0$ kcal. for bromine, and $33.5 + 17.7 = 51.2$ kcal. for the iodine compound.

Reaction d: $CH_2=CHX + HX \rightarrow CH_2=CH_2 + X_2$.

In addition to the bimolecular mechanism, for which activation energies are given in Table II, the following chain is suggested:

$$CH_2=CHX \rightleftarrows \underset{|}{C}H=CH_2 + X, \quad (1)$$

$$X + CH_2=CHX \rightarrow \underset{|}{C}H=CH_2 + X_2, \quad (2)$$

$$\underset{|}{C}H=CH_2 + HX \rightarrow CH_2=CH_2 + X. \quad (3)$$

Here $A = \frac{1}{2}(D_{C-X} + A_{(2)} + A_{(3)})$
$= \frac{1}{2}(78.6 + 24.6 + 16.3) = 59.8$ kcal. for Cl,
and $\frac{1}{2}(58.0 + 15.1 + 10.0) = 41.6$ kcal. for Br,
and $\frac{1}{2}(44.0 + 10.4 + 4.7) = 29.6$ kcal. for I.

Reaction e: $CH_2=CHX + HX \rightarrow CH_2X - CH_2X$.

The activation energies of this reaction, for a bimolecular mechanism, are given in Table II. The following chain mechanism is suggested:

$$CH_2=CHX \rightleftarrows CH_2=\underset{|}{C}H + X, \quad (1)$$

$$X + CH_2=CHX \rightarrow CH_2X - \underset{|}{C}HX, \quad (2)$$

$$CH_2X - \underset{|}{C}HX + HX \rightarrow CH_2X - CH_2X + X. \quad (3)$$

For chlorine and bromine compounds the reverse of (2) is slow compared to (3) and hence $A = A_{(2)} + \frac{1}{2}D_{C-X} = 0 + 39.3 = 39.3$ kcal. for Cl, and $0 + 29.0 = 29.0$ kcal. for Br. For the iodine compound the reverse of (2) is faster than (3) and therefore

$$A = A_{(2)} + A_{(3)} - A'_{(2)} + \tfrac{1}{2}D_{C-X} = 2.2 + 4.7 - 1.2 + 22.0 = 27.7 \text{ kcal.}$$

Reaction f: $CH_2X - CH_2X \rightarrow CH_2=CHX + HX$.

The activation energies for the unimolecular decompositions are given in Table II. No plausible mechanism involving free radicals for the decomposition of $CH_2X - CH_2X$ into the desired products suggests itself. However, as for reaction *b*, the halogen catalyzed decomposition may be considered. For bromine and iodine it is assumed that the following mechanism is operative:

$$X_2 \rightleftarrows 2X, \quad (1)$$

$$X + CH_2X - CH_2X \rightarrow \underset{|}{C}HX - CH_2X + HX, \quad (2)$$

$$\underset{|}{C}HX - CH_2X \rightarrow CHX=CH_2 + X. \quad (3)$$

Here

$A = A_{(2)} + \frac{1}{2}D_{X_2} = 35.5 + 17.7 = 51.2$ kcal. for I,

and $23.4 + 22.6 = 46.0$ kcal. for Br.

For Cl we have the following:

$$Cl_2 \rightleftarrows 2Cl, \quad (1)$$

$$Cl + CH_2Cl - CH_2Cl \rightarrow \underset{|}{C}HCl - CH_2Cl + HCl, \quad (2)$$

$$Cl + \underset{|}{C}HCl - CH_2Cl \rightarrow CHCl=CH_2 + Cl_2. \quad (3)$$

In this case $A = D_{Cl_2} = 57.0$ kcal.

Reaction g: $CH_2=CHX + HX \rightarrow CH_3 - CHX_2$.

According to Markownikoff's rule in organic chemistry the hydrogen atom in this reaction will go to the carbon atom having the greatest number of hydrogen atoms. Hence this reaction should predominate over reaction *e*. However, to the degree of approximation used in these calculations, the activation energy of reactions *e* and *g* are the same. That they are approximately equal is evidenced by the fact that both the symmetrical and the unsymmetrical dihalides are usually found experimentally in any given reaction.

The chain mechanism suggested is similar to that given for *e*:

$$CH_2=CHX \rightleftarrows CH_2=\underset{|}{C}H + X, \quad (1)$$

$$X + CH_2=CHX \rightarrow CH_2 - \underset{|}{C}HX_2, \quad (2)$$

$$CH_2 - \underset{|}{C}HX_2 + HX \rightarrow CH_3 - CHX_2 + X. \quad (3)$$

The activation energies are equal to those given under reaction *e*.

Reaction h: $CH_3 - CHX_2 \rightarrow CH_2=CHX + HX$.

From what has been said about reaction *g* it follows that this decomposition will be of the same nature as that of $CH_2X - CH_2X$. Here also

no satisfactory free radical mechanism suggests itself. However, a halogen catalyzed decomposition mechanism for bromine and iodine is as follows:

$$X_2 \rightleftarrows 2X, \quad (1)$$

$$X + CH_3-CHX_2 \rightarrow \dot{C}H_2-CHX_2 + HX, \quad (2)$$

$$\dot{C}H_2-CHX_2 \rightarrow CH_2=CHX + X. \quad (3)$$

The activation energies are the same as given for the free radical mechanism of reaction *f*.

For Cl the following chain is proposed:

$$Cl_2 \rightleftarrows 2Cl, \quad (1)$$

$$Cl + CH_3-CHCl_2 \rightarrow \dot{C}H_2-CHCl_2 + HCl, \quad (2)$$

$$Cl + \dot{C}H_2-CHCl_2 \rightarrow CH_2=CHCl + Cl_2. \quad (3)$$

Here $A = 57.0$ kcal.

Reaction i: $CH_3-CHX_2 \rightarrow CH_2=CH_2+X_2$.

A reasonable mechanism for this decomposition involves a preliminary splitting out of the halogen, followed by a rearrangement of the ethylidene radical. The formation of X_2 could be imagined to take place when the two halogen atoms come close together as a result of a deformation vibration. The two reactions are as follows:

$$CH_3 \cdot CHX_2 \rightarrow CH_3-CH\langle + X_2, \quad (1)$$

$$CH_3-CH\langle \rightarrow CH_2=CH_2. \quad (2)$$

Reaction (2) probably involves a small activation energy and is quite rapid.[9] Reaction (1) is endothermic 100.2, 70.8, and 52.6 kcal. for Cl, Br, and I, respectively. Hence, according to the above mechanism, the activation energy of reaction *k* is at least 100.2, 70.8 and 52.6 kcal. for Cl, Br, and I, respectively.

Reaction j: $CH_2=CH_2+X_2 \rightarrow CH_3-CHX_2$.

The mechanism suggested for this case is the reverse of that for reaction *i*:

$$CH_2=CH_2 \rightarrow CH_3-CH\langle, \quad (1)$$

$$CH_3-CH\langle + X_2 \rightarrow CH_3-CHX_2. \quad (2)$$

Reaction (2) undoubtedly involves a small activation energy and (1) is accordingly considered the rate determining step. This reaction

[9] F. O. Rice and O. K. Rice, *Aliphatic Free Radicals* (Johns Hopkins Press, 1935), pp. 70, 71, 184.

TABLE III.

	Cl			Br			I		
	Activation Energy			*Activation Energy*			*Activation Energy*		
Reaction	Molecular Mechanism	Free Radical Mechanism	ΔH kcal.	Molecular Mechanism	Free Radical Mechanism	ΔH kcal.	Molecular Mechanism	Free Radical Mechanism	ΔH kcal.
a	25.2	28.5	−55.2	24.4	22.6	−25.8	22.4	20.5	− 7.6
b	80.4	78.6 57.0 (Cl_2 catalyz.)	55.2	50.2	43.1 37.7 (Br_2 catalyz.)	25.8	30.0	27.8 28.1 (I_2 catalyz.)	7.6
c	45.0	43.4	−23.0	47.0	46.0	0.6	54.0	51.2	20.2
d	68.0	59.8	23.0	46.4	41.6	− 0.6	33.8	29.6	−20.2
e	43.5	39.3	−32.2	41.9	29.0	−26.4	36.4	27.7	−27.8
f	75.7	57.0 (Cl_2 catalyz.)	32.2	68.3	46.0 (Br_2 catalyz.)	26.4	64.2	51.2 (I_2 catalyz.)	27.8
g	43.5	39.3	−32.2	41.9	29.0	−26.4	36.4	27.7	−27.8
h	75.7	57.0 (Cl_2 catalyz.)	32.2	68.3	46.0 (Br_2 catalyz.)	26.4	64.2	51.2 (I_2 catalyz.)	27.8
i		100.2	55.2		70.8	25.8		52.6	7.6
j		50.0	−55.2		50.0	−25.8		50.0	− 7.6
k			0			0			0
l			0			0			0

is endothermic 45.0 kcal., and if we consider the reverse reaction to have an activation energy of 5 kcal.[9] the value for (1) becomes 50 kcal. Therefore, with the mechanism assumed, the activation energy of reaction *j* is 50 kcal. in the case of each of the halogens.

Reactions k and l: The activation energies of these reactions have not been calculated, the main reason being that we are primarily interested in this paper in the decomposition of the dihalides rather than in their rearrangements.

The preceding results are summarized in Table III.

Discussion

Several interesting conclusions may be drawn from Table III, but this must be done cautiously. It must be remembered that the calculations apply to rather unusual experimental conditions, namely, the reaction must be carried out in the gas phase (or in solution if the solvent is "inert" and doesn't affect the rate) and in the absence of possible catalysts or inhibitors such as oxygen, water vapor, wall effects, and light. Not many experiments are carried out with all of these conditions controlled, and so it is not always possible to directly compare the calculations with laboratory results. It is also to be realized that many of the conclusions which we shall draw will naturally depend upon the particular mechanisms considered. These mechanisms are of course not necessarily unique, and other schemes may possibly be thought of which give rise to lower activation energies. Kassel[10] has emphasized this point. Also, in the case of chain mechanisms efficient chain breaking reactions may be present under some experimental conditions.

From the scheme given in the introduction it is seen that the halogens may react with ethylene in three different ways, i.e., reactions *a*, *c*, and *j*. From Table III it is clear that reaction *a* is favored in the case of chlorine, bromine, and iodine. This is brought out in Table IV.

$$\mathrm{CH_2{=}CH_2{+}X_2} \xrightarrow{a} \mathrm{CH_2X{-}CH_2X}$$
$$\mathrm{CH_2{=}CH_2{+}X_2} \xrightarrow{c} \mathrm{CH_2{=}CHX{+}HX}$$
$$\mathrm{CH_2{=}CH_2{+}X_2} \xrightarrow{j} \mathrm{CH_3{-}CHX_2}.$$

[10] L. S. Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Company, 1932), p. 118.

Table IV. *Activation energies.*

Reaction	Cl	Br	I
a	25.2	22.6	20.5
c	43.4	46.0	51.2
j	50.0	50.0	50.0

In Table IV the lowest value of the activation energy (molecular or free radical mechanism) is given in each case. The table may not only be used to determine the relative probability of the various possible reactions but also, for any given reaction, the relative reactivity of the three halogens. It is seen that the symmetrical addition of a halogen to ethylene is much more likely than substitution. Also, the bimolecular mechanism is slightly to be preferred in the case of chlorine, whereas the proposed radical mechanism is predominant for bromine and iodine. However, the differences in activation energies are so small that it may well be that both mechanisms are simultaneously operative in each case. Additional remarks concerning the addition of the halogens to ethylene are given in the paper by Sherman and Sun. It was pointed out there that the low activation energy for the addition of iodine to ethylene is in apparent disagreement with the commonly accepted ideas of organic chemistry concerning the reaction. One further piece of experimental evidence qualitatively confirming our calculations is furnished by Cuthbertson and Kistiakowsky[11] who studied the thermal gas phase equilibrium between ethylene iodide, ethylene, and iodine in the temperature range 50–125°C. They found that the equilibrium is established in the course of several hours, and the activation energy required for the addition must be low enough for the reaction to occur in this time and temperature interval.

There have been several experimental studies of the reaction between ethylene and bromine[12–17]

[11] Cuthbertson and Kistiakowsky, J. Chem. Phys. **3**, 631 (1935).
[12] Stewart and Edlund, J. Am. Chem. Soc. **45**, 1014 (1923).
[13] Norrish, J. Chem. Soc. **123**, 3006 (1923).
[14] Davis, J. Am. Chem. Soc. **50**, 2769 (1928).
[15] G. Williams, J. Chem. Soc. 1747, 1758 (1932).
[16] D. M. Williams, ibid. 2911 (1932).
[17] Mitsukuri, Kinumaki and Asaoda, J. Chem. Soc. Japan **54**, 1061 (1933).

TABLE V. *Activation energies.*

Reaction	Cl	Br	I
d	59.8	41.6	29.6
e	39.3	29.0	27.7
g	39.3	29.0	27.7

but the results are complicated. In a glass vessel the reaction apparently occurs on the walls. G. Williams reports that the order of the reaction may be 2, 1, or 0, depending upon the reaction vessel employed. Davis, G. Williams, and D. M. Williams report a negative temperature coefficient for the reaction, the explanation of which can only be furnished by a more detailed treatment than we have presented. G. Williams reports that the substitution reaction was not detected since all attempts to prove the formation of HBr by freezing out the reaction product failed.

Bahr and Zieler[18] and Stewart and Smith[19] report that substitution takes place between ethylene and chlorine but not between ethylene and bromine.

Kinumaki[20] studied the reaction between ethylene and chlorine and reports that a negative temperature coefficient is observed.

The vinyl halides and corresponding hydrogen halides may react in three ways, i.e., reactions *d*, *e*, and *g*. From Table III it is seen that reactions *e* and *g* are favored. This is brought out in Table V.

$$\mathrm{CH_2{=}CHX + HX} \xrightarrow{e} \mathrm{CH_2X{-}CH_2X}$$
$$\mathrm{CH_2{=}CHX + HX} \xrightarrow{d} \mathrm{CH_2{=}CH_2 + X_2}$$
$$\mathrm{CH_2{=}CHX + HX} \xrightarrow{g} \mathrm{CH_3{-}CHX_2}.$$

One thus predicts that the vinyl halides and hydrogen halides will react, by *e* and *g*, to give mixtures of the corresponding ethylidene halides and symmetrical dihalide ethane derivatives, in each case preferably by a free radical mechanism. In the case of the iodine compounds one would also expect some ethylene to be formed since the activation energy for the reaction concerned is only slightly higher.

[18] Bahr and Zieler, Zeits. f. angew. Chem. **43**, 233 (1930).
[19] Stewart and Smith, J. Am. Chem. Soc. **51**, 3082 (1929).
[20] Kinumaki, J. Chem. Soc. Japan **54**, 142 (1933).

TABLE VI. *Activation energies.*

Reaction	Cl	Br	I
b	57.0	37.7	28.1
f	57.0	46.0	51.2

Kharasch, McNab and Mayo[21] studied the reaction between HBr and liquid vinyl bromide and found an addition reaction took place, but the nature of the products depends upon the presence or absence of peroxides, and the reaction is probably heterogeneous.

Kharasch and Hannum[22] report that HCl won't add appreciably to vinyl chloride in the presence or absence of peroxides or under strong illumination, but will do so rapidly in the presence of a catalyst such as $FeCl_3$. This is to be expected, since from Table V it is seen that the activation energy concerned is 39.3 kcal.

Considering, now, the halogen catalyzed decomposition of the CH_2X-CH_2X compounds, we note that the reaction may proceed via *b* to give ethylene and X_2, or via *f* to give vinyl halide and the corresponding hydrogen halide. The results are summarized in Table VI.

$$\mathrm{CH_2X{-}CH_2X} \xrightarrow{b} \mathrm{CH_2{=}CH_2 + X_2}$$
$$\mathrm{CH_2X{-}CH_2X} \xrightarrow{} \mathrm{CH_2{=}CHX + HX}.$$

We see that CH_2Br-CH_2Br and CH_2I-CH_2I would be expected to decompose more rapidly into ethylene and bromine or iodine. The decomposition of CH_2Cl-CH_2Cl must be considered in more detail. Considering the mechanisms proposed it is evident that the slow step in the decomposition via *b* or *f* is the formation of Cl atoms. These atoms now have a choice of picking off a hydrogen atom or a chlorine atom from CH_2Cl-CH_2Cl. From Table II it is seen that the former possibility is to be expected, whereas for the bromine or iodine atoms halogen formation would be predicted. This is brought out in Table VII.

$$\mathrm{X + CH_2X{-}CH_2X} \xrightarrow{1} \mathrm{CH_2{-}CH_2X + X_2}$$
$$\mathrm{X + CH_2X{-}CH_2X} \xrightarrow{2} \mathrm{CHX{-}CH_2X + HX}.$$

[21] Kharasch, McNab and Mayo, J. Am. Chem. Soc. **55**, 2521 (1933).
[22] Kharasch and Hannum, J. Am. Chem. Soc. **56**, 712 (1934).

TABLE VII. *Activation energies.*

Reaction	Cl	Br	I
1	24.6	15.1	10.4
2	14.9	23.4	33.5

Hence one concludes that CH_2Cl-CH_2Cl will give $CH_2=CHCl+HCl$, whereas CH_2Br-CH_2Br and CH_2I-CH_2I will give $CH_2=CH_2+Br_2$ and $CH_2=CH_2+I_2$, respectively. Experimental confirmation of the former conclusion is afforded by the experiments of Boeseken and Bastet.[23]

Arnold and Kistiakowsky[24] studied experimentally the decomposition of $C_2H_4I_2$ and found it to decompose into C_2H_4 and I_2, in agreement with our calculations. They reported that the unimolecular and free radical mechanism are both operative. Ogg[25] later showed that the observed rate expression could be derived by assuming only the radical chain, but this does not mean that some $C_2H_4I_2$ may not be decomposing unimolecularly.

Turning now to the ethylidene halides we have two possible decomposition products, ethylene or vinyl halides. We considered the halogen catalyzed decomposition to give the vinyl compounds but no plausible catalyzed reaction for ethylene formation readily suggests itself. With the schemes considered we see that in the case of each halogen reaction *h* can occur more readily than *i*. However, in the case of the bromine and iodine compounds reactions *e* and *b* have lower activation energies than *h*. Therefore the products of the decomposition of CH_3-CHBr_2 will be C_2H_4 and Br_2, and of CH_3-CHI_2 they will be C_2H_4 and I_2, and it is immaterial whether or not reaction *h* or *i* is more rapid as far as the nature of the decomposition products of these ethylidene halides is concerned.

It is apparent, however, that CH_3-CHCl_2 will give $CH_2=CHCl$ and HCl as decomposition products. With the mechanism assumed reaction *i* is altogether improbable for this compound. There is some experimental evidence that this conclusion is correct.[26]

Although the activation energies of reactions *k* and *l* have not been calculated it turns out that a knowledge of them is not necessary as far as predicting the products of the decomposition of the symmetrical and unsymmetrical dihalide ethane derivatives is concerned. Thus, whether we start out with CH_3-CHX_2 or CH_2X-CH_2X, and whether there is a preliminary rearrangement or not, the final products are ethylene and halogen in the case of bromine and iodine, and in the case of chlorine $CH_2=CHCl$ and HCl.

The scheme given in the introduction, and the preceding discussion, indicate a number of possible mechanisms for the rearrangement of CH_3-CHX_2 into CH_2X-CH_2X. Thus, the formation of CH_2X-CH_2X may occur directly via reaction *k*, or indirectly via reactions *h* followed by *e*, or *i* followed by *a*, or *i* followed by *c* and then *e*, or *h* followed by *d* and *a*. As far as our calculations are concerned we would expect the rearrangement through reactions *h* and *e* to be the most likely, although, of course, the direct reaction *k* may be preferred. It is interesting to note in this connection that in the rearrangement of $CH_3CHBr-CH_2Br$ to give $CH_3-CBr_2-CH_3$ or $CH_3CH_2CHBr_2$ a mechanism involving the splitting out of HBr and its subsequent addition has been postulated.[27]

A few general remarks are now, perhaps, not out of order. It is rather surprising that in so many cases a radical mechanism can be put forth which gives rise to an over-all activation energy which is usually about the same or somewhat lower than the value found for the straight unimolecular or bimolecular reaction. In only one case (reaction *a*, chlorine) is the activation energy for the radical mechanism greater than for the bimolecular reaction, and here by only 3.3 kcal.

It was formerly common for chemical kineticists to regard most reactions as unimolecular or bimolecular. Present day fashion is apparently

[23] Boeseken and Bastet, Rec. trav. chim. **32**, 187 (1914). See also reference 9, p. 138, and C. D. Hurd, *Pyrolysis of Carbon Compounds* (Chemical Catalog Company, 1929), p. 131.

[24] Arnold and Kistiakowsky, J. Chem. Phys. **1**, 166 (1933).

[25] Ogg, J. Am. Chem. Soc. **58**, 607 (1936).

[26] See C. D. Hurd, reference 23, p. 131.

[27] Reference 23.

tending more and more toward free radical mechanisms. However, Table III suggests that, insofar as the reactions there considered are concerned, in many cases both a molecular and a free radical mechanism may be operative. This is brought out in reactions *a* for Cl, Br, and I, *b* for I, *c* for Cl, Br, and I, *d* for Br and I, and *e* for Cl, where the activation energies for the two mechanisms differ by less than 5 kcal.

Conclusions

In the present paper all the arguments concerning the probable course of a reaction, where the reactants may give several different products, are based upon the assumption that the speed of the various reactions determine which products will be formed. This has the advantage of allowing for the possibility of a mixture of products in any proportions (see, for example, reactions *e* and *g*). It was further assumed that the relative rates of several reactions could be predicted from a knowledge of their relative activation energies. This is of course not always safe since the speed of a reaction also depends upon a constant term (the expression for the specific reaction rate constant is taken as $k = \text{constant} \cdot e^{-A/RT}$)[28] and upon the concentration of reacting substances. However since A enters the rate expression exponentially it is usually the most important term, unless it happens to be nearly equal to zero. Particularly if, for example, two reactions differ in activation energy by 6 or more kcal. their relative rates are predictable with considerable probability unless the concentration of some of the reacting substances is exceedingly small. One exception concerning the reliability of relative activation energies must be noted. This is the case where different mechanisms are involved, and different bonds are being broken, such as reactions *a* and *j*, but not, for example, reactions *a* and *b*. In the case of mechanisms involving free radicals it is seen that we have the interesting case that although two reactions have the same over-all activation energy one is much more probable than the other (reaction *b* and *f* for $C_2H_4Cl_2$).

It has been pointed out many times that relative activation energies can be calculated with more assurance than absolute values.[29] In this paper these relative values constitute the basis of all of our conclusions.

It must also be remembered that, strictly speaking, our conclusions only apply at the beginning of a process, when the reaction is far removed from the stage of equilibrium.

In spite of the above difficulties it seems fairly safe to draw the following conclusions:

1. Chlorine, bromine, and iodine will add to ethylene to form 1,2-dihaloethane rather than the vinyl or ethylidene derivatives.
2. The hydrogen halides of chlorine and bromine will add to the corresponding vinyl compounds rather than react to form ethylene and halogen, whereas the iodine compounds will probably undergo both types of reaction.
3. The symmetrical dihalo derivatives and also the ethylidene compounds of bromine and iodine will decompose to give ethylene and the corresponding halogen, whereas 1,2-dichlorethane and ethylidene chloride will give vinyl chloride and HCl upon decomposition.
4. In most of the reactions considered mechanisms involving free radicals are slightly more probable than the corresponding unimolecular or bimolecular reactions.

We wish to express our appreciation to Professor Farrington Daniels for his constant interest and help in this problem. One of us (A. S.) wishes gratefully to acknowledge financial assistance from the Wisconsin Alumni Research Foundation.

[28] For an evaluation of this constant see Eyring, J. Chem. Phys. **3**, 107 (1935). It is also possible that the rate determining step for a reaction involving a proton, may involve a leakage through a potential energy barrier.

[29] See, for example, reference 3.

Errata: The Absolute Rate of Reactions in Condensed Phases

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(J. Chem. Phys. **3**, 492 (1935)

On p. 497, line 12, first column and again in line 14 should read $(\alpha^*)^{-1}$. The values of α for nitromethane and carbon tetrachloride are 0.00233 and 0.00213, respectively. We wish to thank Mr. Frank Brescia for calling this to our attention.

On the Calculation of the Relaxation Effect in Solution of Strong Electrolytes

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DEBYE and Hückel[1] have, as it is known, demonstrated that calculation of the magnitude of the relaxation effect in solutions of strong electrolytes leads, in the most general case of a solution with S types of ions, to the solution of a system of S equation, of the type:

$$\Delta\Delta\psi_j' - \frac{4\pi}{DkT}\sum_i \frac{n_i e_i^2 \omega_i}{\omega_i+\omega_j}\Delta\psi_j' - \frac{4\pi}{DkT}\sum_i \frac{n_i e_i e_j \omega_i}{\omega_i+\omega_j}\Delta\psi_i'$$
$$= \frac{4\pi}{(DkT)^2}\sum_i \frac{\omega_i k_i - \omega_i k_j}{\omega_i+\omega_j} n_i e_i^2 e_j \frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{\varepsilon}\right), \quad (1)$$

where ψ_i' (or ψ_j') is the additional potential at the location of the ith (jth) ion, appearing as a result of destroying the symmetry of the ion atmosphere.

Here

$n_i(n_j)$ is the number of ions of the ith (jth) type, per unit volume.
$e_i(e_j)$—charge on the ith (jth) ion.
$\omega_i(\omega_j)$—reciprocal of coefficient of friction of the ith (jth) ion.
$\mathbf{k}_i(\mathbf{k}_j)$—strength of the external field acting on the ith (jth) ion.
D—dielectric constant of the solvent.
k—Boltzmann constant.
T—absolute temperature.

$$\kappa^2 = \frac{4\pi}{DkT}\sum_i n_i e_i^2$$

and Δ signifies the Laplacian operator.

The system of Eqs. (1) can be solved by the usual differential equation methods, only for $S=2$, i.e., when the solution contains a single binary electrolyte.

Onsager and Fuoss[2] have shown, however, that by use of matrix algebra, this system can be solved, in its most general form. The solution for the additional potential found by them, in the form of a matrix function, comes out to be:

$$\text{grad}_x\psi_j' = (1/3DkT)(\kappa - C^{\frac{1}{2}})_{j\sigma} e_\sigma \mathbf{k}_\sigma, \quad (2)$$

where C is a matrix with the components

$$C_{ji} = \frac{4\pi}{DkT}\left(\frac{n_\sigma e_\sigma^2 \omega_\sigma}{\omega_\sigma+\omega_j}\delta_{ji} + \frac{n_i e_i e_j \omega_i}{\omega_i+\omega_j}\right) \quad (3)$$

and σ indicates summation over all values of i. δ_{ji} is the Kronecker index, which is equal to unity when $i=j$, and to zero when $i\neq j$.

That is $$\delta_{ji} = \begin{cases} 1, & \text{if } i=j \\ 0, & \text{if } i\neq j. \end{cases}$$

For the case when the concentration of the solution is homogeneous, $\mathbf{k}_i = Xe_i$; and $\text{grad}_x\psi_j' = -\Delta X_j$, where X is the strength of the external electric field. Substituting this expression into (2), and dividing both sides of (2) by X, we obtain the magnitude of the relaxation effect in the form

$$-(\Delta X_j/X) = (1/3DkT)(\kappa - C^{\frac{1}{2}})_{j\sigma} e_\sigma^2$$
$$= (\epsilon^2\kappa/3DkT)\sum_i (1-\kappa^{-1}C^{\frac{1}{2}})_{ji} z_i^2. \quad (4)$$

Calling $z_i^2 = \delta_{ji} z_j^2$, (4) can be written as follows:

$$-(\Delta X_j/X) = (\epsilon^2\kappa/3DkT) z_j \sum_i (1-\kappa^{-1}C^{\frac{1}{2}})_{ji}\delta_{ji} z_j \quad (5)$$

The next step in calculating the magnitude of the relaxation effect for a mixture of electrolytes consists of transforming the matrix function (5) to simple figures.

Onsager and Fuoss[2] proposed to accomplish this transformation by expanding the matrix function in a Taylor series, and determining the convergence of the series. This method turns out to be very long and complicated. Evaluation of $\Delta X_j/X$ can be accomplished by a much simpler and shorter method, using the Lagrange-Sylvester equation,[3] by letting any matrix function appear as a finite matrix polynomial, with a number of terms equal to the order of the matrix, n, and having its highest power equal to $(n-1)$.

[1] Debye and Hückel, Physik. Zeits. **24**, 305 (1923).
[2] Onsager and Fuoss, J. Phys. Chem. **36**, 2689 (1932).
[3] Lappo-Danilevski, *Theory of Matrix Function and System of Linear Differential Equations* (1932), p. 32.

The Lagrange-Sylvester equation is as follows:

$$f(x)=\sum_{k=1}^{k=n}\frac{(x-\epsilon_1)\cdots(x-\epsilon_{k-1})(x-\epsilon_{k+1})\cdots(x-\epsilon_n)}{(\epsilon_k-\epsilon_1)\cdots(\epsilon_k-\epsilon_{k-1})(\epsilon_k-\epsilon_{k+1})\cdots(\epsilon_k-\epsilon_n)}f(\epsilon_k), \tag{6}$$

where ϵ_1, ϵ_2, $\epsilon_3\cdots\epsilon_n$ are characteristic numbers of the matrix x, found by solution of the characteristic equation.

Applying the Lagrange-Sylvester equation to the function $(1-\kappa^{-1}C^{\frac{1}{2}})$ the latter can be written in polynomial form:

$$(1-\kappa^{-1}C^{\frac{1}{2}})=\sum_{k=1}^{k=s}\frac{(C-\epsilon_1)\cdots(C-\epsilon_{k-1})(C-\epsilon_{k+1})\cdots(C-\epsilon_s)}{(\epsilon_k-\epsilon_1)\cdots(\epsilon_k-\epsilon_{k-1})(\epsilon_k-\epsilon_{k+1})\cdots(\epsilon_k-\epsilon_s)}(1-\kappa^{-1}\epsilon_k^{\frac{1}{2}}). \tag{7}$$

And according to (5), for determining $\Delta X_j/X$, with the i, jth element of the polynomial of degree $(S-1)$ and of S terms, it is necessary to operate on the vector z_i.

Thus, the method of evaluating $\Delta X_j/X$ for a mixture of electrolytes, using the Lagrange-Sylvester equation, can be formulated as follows:

1. The matrix C is formed.
2. The characteristic numbers of the matrix C are found by solution of the characteristic equation (the degree of which is equal to the order of the matrix).
3. The function $(1-\kappa^{-1}C^{\frac{1}{2}})$ is written in the form of the Lagrange-Sylvester polynomial.
4. According to (5), vector z_i is operated on by the j, ith element of this polynomial.

Sample Calculations

1. For $S=2$, i.e., for the case of a solution containing one binary electrolyte, solution is possible in the general form:

Let n_1=no. of ions of the first kind, per unit volume.

Let n_2=no. of ions of the second kind, per unit volume.

According to (3), the matrix C can be expressed for this case as follows:

$$C=\begin{vmatrix}C_{11} & C_{12}\\ C_{21} & C_{22}\end{vmatrix}=\begin{vmatrix}\frac{4\pi}{DkT}\left[n_1e_1^2+\frac{n_2e_2^2\omega_2}{\omega_1+\omega_2}\right]; & \frac{4\pi}{DkT}\left[\frac{n_2e_1e_2\omega_2}{\omega_1+\omega_2}\right]\\ \frac{4\pi}{DkT}\left[\frac{n_1e_1e_2\omega_1}{\omega_1+\omega_2}\right]; & \frac{4\pi}{DkT}\left[n_2e_2^2+\frac{n_1e_1^2\omega_1}{\omega_1+\omega_2}\right]\end{vmatrix}. \tag{8}$$

Characteristic equation:

$$\epsilon^2-(C_{11}+C_{22})\epsilon+(C_{11}C_{22}-C_{12}C_{21})=0. \tag{9}$$

Substituting in (9) the expression for C_{11}, C_{22}, C_{12}, C_{21} from (8), and for simplification introducing the factor

$$q=(n_1e_1^2\omega_1+n_2e_2^2\omega_2)/[(n_1e_1^2+n_2e_2^2)(\omega_1+\omega_2)] \tag{10}$$

and solving Eq. (9), we obtain the characteristic numbers: $\epsilon_1=\kappa^2$; $\epsilon_2=q\kappa^2$. Knowing the characteristic numbers it is possible, according to (7), to write $(1-\kappa^{-1}C^{\frac{1}{2}})$ in the form of the following polynomial:

$$(1-\kappa^{-1}C^{\frac{1}{2}})=(\kappa^2-C)/(\kappa^2(1+\sqrt{q})). \tag{11}$$

Then, according to (5), we must set up

$$\sum_i(1-\kappa^{-1}C^{\frac{1}{2}})_{ji}z_i=\sum_i\left[\frac{\kappa^2-C}{\kappa^2(1+\sqrt{q})}\right]_{ji}z_i$$

$$=\sum_i\left(\frac{1}{1+\sqrt{q}}\delta_{ji}z_i-\frac{1}{\kappa^2(1+\sqrt{q})}C_{ji}z_i\right)$$

$$=\frac{z_j}{1+\sqrt{q}}-\frac{1}{\kappa^2(1+\sqrt{q})}(C_{j1}z_1+C_{j2}z_2). \tag{12}$$

Inserting in (12), for C_{j1} and C_{j2}, the elements of the jth column of the matrix C (8), we obtain:

$$(1-\kappa^{-1}C^{\frac{1}{2}})_{j\sigma}z_\sigma=(q/1+\sqrt{q})z_i.$$

Consequently,

$$\Delta X_j/X=(\epsilon^2\kappa/3DkT)(q/(1+\sqrt{q}))z_iz_j \quad (13)$$

(the result already arrived at in the earlier work of Onsager).

For the case of $S>2$, the general solution becomes too cumbersome and the final equations become difficult to grasp, so that it is simpler to carry out a complete calculation for a given solution of mixed electrolytes.

Let us take for example* calculation of the magnitude of the relaxation effect for a mixture of 2 electrolytes, HCl and KCl, containing 0.04995 mole of HCl and 0.05016 mole of KCl, in a liter of water solution at 18°C.

We determine the magnitude of $\Delta X_j/X$ for each kind of ions:

Ion	j	Λ_j^0	$\mu_i=\frac{n_ie_i^2}{n_\sigma e_\sigma^2}$	$\omega_{ij}=\frac{\omega_i}{\omega_i+\omega_j}=\frac{\Lambda_i^0}{\Lambda_i^0+\Lambda_j^0}$	
H^+	1	315	0.2495	$\omega_{12}=0.8298$	
K^+	2	64.6	0.2505	$\omega_{23}=0.4965$	$\omega_{jj}=\frac{1}{2}$
Cl^-	3	65.5	0.5000	$\omega_{13}=0.8279$	

Using the expression $\mu_i=n_ie_i^2/n_\sigma e_\sigma^2$ and $\omega_{ij}=(\omega_i/(\omega_i+\omega_j))=(\Lambda_i^0/(\Lambda_i^0+\Lambda_j^0))$ the element of the matrix can be rewritten as:

$$C_{ji}=\kappa^2(\delta_{ji}\sum_i\mu_i\omega_{ij}+\mu_i\omega_{ij}).$$

For this case, matrix C will be expressed as follows:

$$\begin{vmatrix} 0.3782\kappa^2 & 0.2070\kappa^2 & 0.2066\kappa^2 \\ 0.0426\kappa^2 & 0.7094\kappa^2 & 0.1244\kappa^2 \\ 0.0860\kappa^2 & 0.2518\kappa^2 & 0.8310\kappa^2 \end{vmatrix}. \quad (14)$$

Characteristic equation:

$$(\epsilon/\kappa^2)^3-1.9186(\epsilon/\kappa^2)^2+1.1142(\epsilon/\kappa^2)-0.1956=0.$$

* Example from the work of Fuoss and Onsager.

Characteristic numbers:

$$\epsilon_1=\kappa^2, \quad \epsilon_2=0.5832\kappa^2, \quad \epsilon_3=0.3354\kappa^2, \quad (15)$$

$$(1-\kappa^{-1}C^{\frac{1}{2}})_{j\sigma}z_\sigma=\left[\frac{(C-\epsilon_2)(C-\epsilon_3)}{(\epsilon_1-\epsilon_2)(\epsilon_1-\epsilon_3)}(1-\kappa^{-1}\epsilon_1^{\frac{1}{2}})+\frac{(C-\epsilon_1)(C-\epsilon_3)}{(\epsilon_2-\epsilon_1)(\epsilon_2-\epsilon_3)}(1-\kappa^{-1}\epsilon_2^{\frac{1}{2}})+\frac{(C-\epsilon_1)(C-\epsilon_2)}{(\epsilon_3-\epsilon_1)(\epsilon_3-\epsilon_2)}(1-\kappa^{-1}\epsilon_3^{\frac{1}{2}})\right]_{j\sigma}z_\sigma$$

or, substituting for ϵ_1, ϵ_2 and ϵ_3 their values from (15)

$$(1-\kappa^{-1}C^{\frac{1}{2}})_{j\sigma}z_\sigma=(1/\kappa^4)(0.2679C^2-0.99106C\kappa^2+0.72316\kappa^4)=(0.2679/\kappa^4)C_{j\sigma}{}^2z_\sigma-(0.99106/\kappa^2)C_{j\sigma}z_\sigma+0.72316z_i. \quad (16)$$

Expressing this polynomial for each j, and bearing in mind that for the given example $z_1=z_2=1$, and $z_3=-1$, the value of $(1-\kappa^{-1}C^{\frac{1}{2}})_{j\sigma}z_\sigma$ can be found.

The calculations have shown the following results:

Ion	j	$z_j(1-\kappa^{-1}C^{\frac{1}{2}})_{j\sigma}z_\sigma$ (Our calculation)	$z_j{}^1\Sigma C_nz_j{}^{(n)}$ (Values from Onsager and Fuoss)
H^+	1	0.4213	0.4212
K^+	2	0.1757	0.1758
Cl^-	3	0.2982	0.2982

The results thus agree perfectly with those of Onsager and Fuoss, but the method of calculation is considerably simpler than that proposed by them.

The author would like to express her appreciation to M. N. Olevski and V. A. Pleskov for valuable assistance in carrying out this work.

Errata: Exchange of Energy Between Organic Molecules and Solid Surfaces

Part I. Accommodation Coefficients and Specific Heats of Hydrocarbon Molecules

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(J. Chem. Phys. **4**, 680 (1936))

IN line 11 of the abstract read "constant volume" instead of "constant pressure."

The last term in brackets of the first part of Eq. (2) should read $\frac{3}{4}\left(Cv-\frac{3R}{2}\right)$ instead of $\frac{3}{4}\left(Cv-\frac{R}{2}\right)$.

Eq. (10) is arrived at from Eq. (8), not (5), and the double parenthesis should enclose the whole expression before the last term.

The Absolute Rate of a Chemical Reaction: The Formal Thermodynamic Treatment

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In order to assign a definite value to the entropy of activation, it is necessary to make definite assumptions as to the topography of the energy surface traversed by the reacting system. When this is done, the entropy of activation becomes the difference between the entropy of the average molecule and the entropy of the activated complex at the steady state concentration required for unit rate of reaction. The racemization of diphenyl derivatives is considered as a special case of unimolecular reaction where $h\nu \ll kT$.

SOME years ago the author published a discussion of the relation between thermodynamics and the absolute rate of a gaseous chemical reaction.[1] Since then the subject has been discussed by Polanyi, Eyring, Rice, and collaborators in great detail.[2] Most of these treatments have used the methods of statistical mechanics. They have gone beyond the simple kinetic theory of collisions between molecules in that they have introduced assumptions as to the topography of energy barriers which have yielded more specific results. These treatments are certainly adequate, and may be criticized only as to style of presentation. The treatments are perhaps unavoidably rather difficult to follow. On the other hand, the final results may appear too simple, since complicated functions are concealed in simple symbols.

The author[1] has stated that he felt that the thermodynamic approach was at once more simple and more general, and wishes to point out some conclusions from this method by way of clarification and comment. In his original treatment, he discussed the Arrhenius equation

$$k = Ae^{-Q/RT} \tag{1}$$

and pointed out that the constant A could be identified formally with an entropy of activation ΔS, just as Q was the heat of activation. He discussed the case of a unimolecular dissociation. It followed from his treatment that the molecule which was on the point of dissociation (the "activated complex") could be assigned formally an entropy in the significant degree of freedom of kT/h. This entropy could not be given any real significance, however, without further assumptions as to the interatomic forces which lie entirely outside of thermodynamics.

In 1923 the author[3] had made the assumption that a unimolecular dissociation took place by the acquirement of a critical energy in a certain significant degree of freedom, and that when this energy was acquired, the molecule would dissociate at the end of the vibration. This assumption has been generalized by Polanyi and Eyring in the postulates that the crest of the energy barrier to be traversed is nearly flat and that the chance of reflection at the barrier is small.

The first of these postulates is probably a good approximation except in the case of predissociations. The second is not likely to lead to serious error, since the reflection coefficient will probably not be greater than one-half. A value of one-half may be anticipated in case the energy barrier has a basin, as has been calculated by Eyring. The existence of this basin is in accord with the picture that was in the author's mind when he wrote the former paper, since he supposed the activated complex to have a degree of stability, and equal probability of a transformation in either direction.

The procedure is then very simple. From the rate of disappearance of the activated molecules, one calculates the steady state concentration of these molecules. At unit rate of reaction, the entropy of activation is then the difference between the entropy of the activated molecules at their steady state concentration and the entropy of all other molecules at unit concentra-

[1] W. H. Rodebush, J. Chem. Phys. **1**, 440 (1933).

[2] H. Eyring, J. Chem. Phys. **3**, 107 (1935); Evans and M. Polanyi, Trans. Faraday Soc. **21**, 875 (1935); O. K. Rice and H. Gershinowitz, J. Chem. Phys. **2**, 857 (1934); see also V. K. La Mer, J. Chem. Phys. **1**, 289 (1933).

[3] W. H. Rodebush, J. Am. Chem. Soc. **45**, 606 (1923).

tion. This entropy difference involves one degree of freedom only. The heat of activation is known from other data, and the rate constant is thus completely determined.

Let us consider as an example the dissociation of the diatomic molecule which was discussed in the original article.

$$A_2 = 2A. \tag{2}$$

In the familiar potential energy diagram for a diatomic molecule, a point moving on this curve represents the internuclear distance and the molecule may be said to be completely dissociated when this point lies on the flat part of the curve. The number of activated molecules is the number having energy in excess of the dissociation energy. The rate of dissociation R is given by the equation

$$R = k_1 n = c\bar{v}. \tag{3}$$

k_1 is the rate constant, and n the total concentration of molecules. On the other hand, c is the concentration of activated molecules whose internuclear distances lie within a unit interval $r_0 - 1 < r < r_0$, where r_0 is the distance for complete dissociation and $\bar{v}$ is the rate at which the atoms of the molecule move apart. If we make use of the graphical representation referred to above, c is the *linear concentration* of points on the flat crest of the energy curve and $\bar{v}$ is the rate at which these points traverse this curve. A simple application of kinetic theory shows that

$$\bar{v} = (kT/2\pi\mu)^{\frac{1}{2}}, \tag{4}$$

where μ is the reduced mass of the molecule.

We may write from Eqs. (3) and (4)

$$\ln k_1 = \ln (c/n) + \ln (kT/2\pi\mu)^{\frac{1}{2}}. \tag{5}$$

Since c and n are assumed to be in statistical equilibrium

$$\ln (c/n) = -(Q/RT) + (Sc/R) - (Sn/R). \tag{6}$$

Here Q is the heat of activation, as usually defined, and Sc and Sn are the entropies of the activated and unactivated molecules at unit concentration. These entropies differ only in the vibrational degree of freedom, and we may, therefore, write, except for some constants which may be absorbed in the Q/RT term,

$$\ln k_1 = -(Q/RT) + \ln (2\pi\mu kT/h^2)^{\frac{1}{2}} + \ln (kT/2\pi\mu)^{\frac{1}{2}} - Sv, \tag{7}$$

where Sv is the vibrational energy of the unactivated molecules. We may now remember that the entropy of the activated molecules is for unit concentration in (7), so that the term $\ln (1/c)$ does not appear in the second term of (7). At unit rate of reaction (one molecule per second), however, $1/c$ is equal to $(kT/2\pi\mu)^{\frac{1}{2}}$. Hence, if we combine the second and third terms of (7), we obtain $\ln (kT/h)$.

Except for the constant term mentioned above, this is $1/R$ times the entropy of the activated molecules at such a concentration as to bring about unit rate of reaction. Hence, we may write

$$\ln k_1 = -Q/RT + \Delta S^*/R, \tag{8}$$

where ΔS^* is the entropy of activation as defined earlier in this paper.

If the vibrational quantum of the dissociating molecule is small so that $h\nu \ll kT$, then Sv/R of Eq. (7) becomes $\ln (kT/h\nu)$ and $\Delta S^*/R$ becomes equal to $\ln \nu$. Thus, Eq. (1) becomes

$$k_1 = \nu e^{-Q/RT}, \tag{9}$$

as was pointed out by the author in his earlier publication. For this condition to obtain, however, at 298°, ν must not be greater than 10^{11}, which is, of course, an extremely low vibrational frequency, and which is likely to be associated only with a very small heat of dissociation.

If ν is larger, so that $h\nu$ is comparable or greater than kT, then the term Sv becomes so small as to be negligible, and Eq. (1) becomes

$$k_1 = (kT/h)e^{-Q/RT} \tag{10}$$

as obtained by Eyring.

For the temperature interval in which unimolecular dissociations have been studied kT/h is of the order of magnitude 10^{13}, and one reaches the surprising conclusion that the constant of a unimolecular dissociation reaction cannot be greater than this figure. One might suppose, of course, that a fundamental error had been made in estimating the entropy of a fugitive complex where the quantization cannot be sharp because of the short life period. So far as experiment shows, however, there is no certain contradiction of the above figure. All cases in which the con-

stant A of Eq. (1) is larger than 10^{13} may be explained as due either to the possibility of dissociation in several different degrees of freedom, as is the case with nitrogen pentoxide, or simply to experimental error. When the results of an experimental determination of k_1 are plotted on a $\log k - 1/T$ diagram one sees what a small interval the results cover. The heat of activation may be determined as a satisfactory approximation from the slope of the curve, but the constant A is the intercept on the $\log k_1$ axis and requires a long extrapolation. A slight error in the slope produces a very large error in k_1.

The one example which has come to the author's attention where the frequency is small so that Eq. (9) holds is the racemization of diphenyl derivatives. This case also illustrates the point made by the author[4] that the heat of activation may be calculated from measurements at a single temperature.

The racemization of diphenyl derivatives has been studied by Adams and collaborators[5] in various solvents. It has been demonstrated in the case of nitrogen pentoxide that the reaction rate in inert solvents is not greatly different from that in the vapor phase, and we may assume that the same will be true for the racemization of diphenyl.

The racemization of an optically active compound is an example of a reversible first-order reaction for which the constant is given by the expression

$$k_1 = (1/2t) \ln (\alpha_0/\alpha).$$

This constant, in turn, is given by the Arrhenius relation (1).

The best data of Li and Adams appear to be upon 2-nitro-6-carboxy-2′-ethoxydiphenyl. From these data, we calculate

$$Qi = 21{,}150 \text{ cal.}, \quad A = 3.0 \times 10^{11}.$$

This calculation involves the usual difficulty of a calculation of heat of activation in that with the accuracy of the experimental results obtainable, there is an uncertainty of several hundred calories in the heat of activation. Thus, the rates of racemization of the methoxy and propoxy derivatives show about the same temperature coefficients as the ethoxy derivatives, and all that the authors could state was that the heats of activation were the same for the three compounds within the limits of experimental error. This in spite of the fact that the absolute rates of racemization differed by several fold.

Now we are not so much interested in the absolute value of the heats of activation as the differences in different compounds. The heat of activation is presumably the work of turning the diphenyl rings relative to each other when in the plane position. The constant A is the frequency of vibration multiplied by an *a priori* factor which is probably not greatly different from unity. This vibration is a partial rotation of the rings relative to each other about the common axis of symmetry. The value obtained for A, 3×10^{11}, appears to be the order of magnitude to be expected for this sort of vibration. This frequency will vary inversely as the square root of the frequency of the moment of inertia and directly as the square root of the constraint. The constraint is due to the interference of the substituted group, and may be expected to increase with an increase in the heat of activation. The replacement of methoxy by an ethoxy group would increase both the moment of inertia and the constraint, and leave the frequency almost unchanged. We shall, therefore, assume as a first approximation that the constant A is the same for all compounds and calculate the "relative" heats of activation. We obtain

Derivative	Heat of Activation
OCH_3	20,150
OC_2H_5	21,150
OC_3H_7	21,350

From the paper of Hanford and Adams, we obtain for the 4′ substituted diphenyls the following values for the relative heats of activation.

Derivative	Heat of Activation
CH_3	19,350
Cl	19,900
Br	20,350

There can be little doubt that these figures give us the significant variations in the heats of activation in the different derivatives.

[4] W. H. Rodebush, J. Chem. Phys. **3**, 242 (1935).
[5] C. C. Li and Roger Adams, J. Am. Chem. Soc. **57**, 1565 (1935); W. E. Hanford and Roger Adams, J. Am. Chem. Soc. **57**, 1592 (1935).

Note: The $^3\Pi_{1u}$ State and the Absorption Continuum of the Bromine Molecule

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AS is well known the discrete band absorption spectrum of Br_2 consists of two systems, one of which, the main system, occurs between 5110A and 6590A and the other, the extreme red system, between 6450A and 7600A.[1] These systems are attributed, respectively, to the electronic transitions $^3\Pi_{0+u}\leftarrow{}^1\Sigma_g^+$ and $^3\Pi_{1u}\leftarrow{}^1\Sigma_g^+$. The vibrational and rotational constants and the numerations of the common lower state and the upper state of the main system are known fairly accurately but as no measurements of the vibrational isotope effect and no rotational analysis in the case of the extreme red system has been recorded as yet the existing data for the upper state of this system are very incomplete. The data tabulated by Jevons[2] and by Sponer[3] are based on Brown's provisional numeration and are not corrected for Brown's suggested possible increase of 4 ± 2 units in v'.

As a preliminary to the interpretation of a number of diffuse ultraviolet bands in the Br_2 emission spectrum which I have photographed I have attempted, by raising the absorbing vapor to higher temperatures than was done by Brown, to photograph and measure bands of the extreme red system due to transitions from higher v'' levels to lower v' levels than those already recorded. It was hoped thereby to observe measurable isotope head separations and thence to determine the true quantum numeration. As a more complete knowledge of the $^3\Pi_{1u}$ state is necessary for the interpretation of the continuous absorption spectrum recently examined by Acton, Aickin and Bayliss[4] and discussed by Mulliken[5] a brief account of my results and a few comments insofar as they are related to the continuous spectrum may be of interest.

In spite of the very considerable increase in vapor temperature (450°C, cf. 100°C (Brown)) only two new $\Delta G'(v+\frac{1}{2})$ values and three new $\Delta G''(v+\frac{1}{2})$ values were obtained. The region in which it had been hoped that an extension would appear is occupied by seven new short v' progressions ($v''=8$ to $v''=14$) of the main system which after being unobservable in the region occupied by the extreme red system between 6600A and 7100A reappears, coexists with and then above 8180A extends beyond the observed extreme red system. A precise determination of the true numeration has not been effected as only three isotope heads have been measured with reasonable certainty. From them a most probable numeration increase n of 7 units with a possible error of ±2 is predicted. This proposed increase is supported by other considerations relating to (1) the position which the upper P. E. curve must occupy with respect to the lower to account for the nonappearance of the $v''=0$ progression or, if this is not due to dissociation, to account for the close proximity of the predicted intensity maximum in this progression to the system convergence, (2) observation of the sharpest head in a progression it being assumed that for the corresponding band the isotopic separation is least. If Brown's provisional numeration is increased by 7 units the vibrational constants of the bromine molecule in the excited state of the extreme red system are as follows: $\omega_e'=170.7$ cm^{-1}, $x_e'\omega_e'=3.694$, $\nu_e=13{,}814$ cm^{-1}, $\nu^{00}{}_{\text{head}}=13{,}737$ cm^{-1}, $\nu^0{}_{\text{con.}}=15{,}920$ cm^{-1}, $D_0'=2180$ cm$^{-1}=0.269$ ev. This value of D_0' is almost twice as great as that quoted by Jevons and by Sponer, *viz.* 0.144 ev. From the empirical law $\omega_e''r_e''^p=\omega_e'r_e'^p r_e'$ is found to be 2.64A.

Acton, Aickin and Bayliss have found that the absorption continuum of Br_2 in the visible due to transitions from $v''=0$ may be supposed to consist of two unresolved maxima, a strong one A at 24,100 cm^{-1} and a weaker one B at 20,400 cm^{-1}. For transitions from $v''=1$ there are three maxima at 27,000 cm^{-1}, 22,000 cm^{-1} and 19,000 cm^{-1}. They have offered two alternative explanations *viz.* that A and B are due, respectively, to (1) $^3\Pi_{0+u}\leftarrow{}^1\Sigma_g^+$ (main), $^3\Pi_{1u}\leftarrow{}^1\Sigma_g^+$ (ext. red) or (2) $^1\Pi\leftarrow{}^1\Sigma_g^+$ (unobserved, $^1\Pi$ being a theoretically

[1] W. G. Brown, Phys. Rev. **38**, 1179 (1931); **39**, 777 (1932).
[2] W. Jevons, *Report on Band Spectra* (1932).
[3] H. Sponer, *Molekülspektren*, vol. 1 (1935).
[4] A. P. Acton, R. G. Aickin and N. S. Bayliss, J. Chem. Phys. **4**, 474 (1936).
[5] R. S. Mulliken, J. Chem. Phys. **4**, 620 (1936).

predicted repulsive state), $^3\Pi_{0+u} \leftarrow {}^1\Sigma_g^+$ (main). Their discussion is based on predictions from Morse P. E. curves and in both cases they find it necessary to shift the $^3\Pi_{1u}$ curve (plotted evidently on the basis of the provisional numeration) so that r_e' becomes 2.6A "which is considerably less than would be predicted by the usual empirical rules" (2.9A). This difficulty is not removed by the proposed numeration amendment leading to a value of $r_e' = 2.64$A for the necessary deepening of the curve has not been taken into account in their calculations. Explanation (1) receives little or no support from the wave mechanics formulation of the Franck-Condon principle when the more correct Morse $^3\Pi_{1u}$ curve is drawn. The assignment in explanation (2) of the B maximum, 20,400 cm^{-1} to $^3\Pi_{0+u} \leftarrow {}^1\Sigma_g^+$ is well supported for the predicted maximum is at 20,500 cm^{-1}. The $^3\Pi_{1u}$ curve corresponding to a numeration increase of $n=8$ crosses the $^3\Pi_{0+u}$ curve very near $r' = 2.28\text{A} = r_e''$. On this basis B is composite, the main and extreme red maxima coinciding very near 20,500 cm^{-1}. This is in harmony with Mulliken's suggested modification of explanation (2) and it becomes unnecessary to suppose as do A. A. and B. that the $^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+$ continuum lies farther to the red in a region they were unable to examine.

There is one other possible explanation suggested by the application of the Franck-Condon principle. For $n=6$ the extreme red maximum should occur at 23,400 cm^{-1} and for $n=5$ at 24,700 cm^{-1} and so maximum A might be due to $^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+$. The transition assignments of explanation (1) would then be interchanged. The greater intensity of maximum A is not in this case as readily understood as in explanation (2) and one must suppose that the maximum due to $^1\Pi \leftarrow {}^1\Sigma_g^+$ is outside the range of A. A. and B.'s measurements.

A. A. and B. do not correlate the three $v''=1$ maxima with Franck-Condon predictions. One of them at 27,000 cm^{-1} may be identified with $^3\Pi_{0+u} \leftarrow {}^1\Sigma_g^+$ for which the predicted position is 26,500 cm^{-1}. One of the others 19,000 cm^{-1} and 22,000 cm^{-1} may be due to $^1\Pi \leftarrow {}^1\Sigma_g^+$ but not both since the repulsive state curve would cross the $^3\Pi_{0+u}$ and $^3\Pi_{1u}$ ($n=8$) curves near their intersection and maximum B would be composed of contributions from all three transitions leaving A entirely unaccounted for.

It appears that none of the explanations accounts completely for all five observed maxima. More accurate knowledge of the $^3\Pi_{1u}$ state as regards numeration and the value of r_e' is essential for the unambiguous prediction of maxima. To this end preparations are now being made in this department for the high resolution photography and rotational analysis of the extreme red system.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Hindered Rotation of the Methyl Groups in Ethane

A reliable value of the entropy of ethane from calorimetric measurements extending to 15°K has been obtained by Witt and Kemp.[1] Several investigators[2, 3] have given the treatment for obtaining the entropy of ethane from statistical-mechanical considerations, assuming a model with freely rotating methyl groups. The value of the entropy of ethane obtained from such a treatment, however, differs from the experimental value by 1.57 E.U. The reason for this disagreement could be either the assumption of an incorrect molecular model or an incorrect experimental entropy due to the persistence of rotation in the crystal at low temperatures, as suggested by Aston and Messerly[4] and Kassel[3] for disagreements in the values for other hydrocarbons.

A further discrepancy has been found between an accurate determination of the heat of hydrogenation of ethylene by Kistiakowsky and co-workers,[5, 6] and a large number of concordant experiments on the free energy of hydrogenation of ethylene Using a model of ethane requiring free rotation of the methyl groups, Teller and Topley[7] and Smith and Vaughan,[8] have been unable to correlate these data by a statistical-mechanical calculation. The assumption that ethane rotates in the crystal at low temperatures would not remove this discrepancy.

Confronted with these disagreements, we felt that the trouble lay perhaps in the assumption of completely free rotation of the methyl groups. Accordingly, we have made statistical-mechanical calculations[9] assuming various potential barriers of the form $\frac{1}{2}V_0(1-\cos 3\phi)$. Table I gives a preliminary survey of the results of these calculations, together with the experimental values of the entropy of ethane and the heat of hydrogenation of ethylene.

The values of $\Delta H_{288°}$ calculated for the reaction $C_2H_4+H_2=C_2H_6$ were obtained using the best value of the free energy of reaction selected by Teller and Topley.[7] It is seen that agreement between the various data is obtained only for a potential barrier of about 3150 cal., which, with suitable selection of the uncertain vibration frequency, we have found to be in accord with the heat capacity of ethane gas determined by Eucken and co-workers.[10, 11]

TABLE I. *The heat of hydrogenation of ethylene and the entropy of ethane.*

Calc. with	$\Delta H_{288°}$ (cal.)	$S_{184.1°K}$ (1 atmos.) cal./deg./mole
$V_0=0$ cal.	$-31{,}500\pm300$	51.21 ± 0.2
$V_0=315$ cal.	$-31{,}560\pm300$	51.10 ± 0.2
$V_0=3150$ cal.	$-32{,}940\pm300$	49.44 ± 0.2
experimental	$-32{,}824\pm50$[5]	49.64 ± 0.15[1]

In view of these considerations, we feel that the entropies of ethane and similar hydrocarbons obtained with the aid of the third law of thermodynamics from calorimetric data extending to low temperatures are the correct ones for use in thermodynamic calculations. Thus the disagreements found by Aston and Messerly[4] for tetramethylmethane and by Kassel[3] for *n*-butane are due probably to an incorrect assumption of completely free rotation of the methyl groups. A potential barrier of 3150 cal. in no way conflicts with the existing knowledge of organic chemistry concerning isomerism.

A more detailed discussion of both the experimental data and statistical-mechanical calculation will be published later.

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[1] To be published.
[2] Mayer, Brunauer and Mayer, J. Am. Chem. Soc. **55**, 37 (1933).
[3] Kassel, J. Chem. Phys. **4**, 276 (1936).
[4] Aston and Messerly, J. Chem. Phys. **4**, 391 (1936).
[5] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughn, J. Am. Chem. Soc. **57**, 65 (1935).
[6] Kistiakowsky, Ruhoff, Smith and Vaughn, J. Am. Chem. Soc. **58**, 137 (1936).
[7] Teller and Topley, J. Chem. Soc. 876 (1935).
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[9] A quantum-mechanical treatment of this model has been given by Nielsen, Phys. Rev. **40**, 445 (1932).
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Infrared Evidence for the Existence of Hydrogen Bonds

The possibility of the formation of hydrogen bonds has been emphasized by many recently.[1] Acetic and formic acids, most of the alcohols, water and some other substances, because of their unusual thermodynamic behavior and their high dielectric constants, are generally supposed to be associated, possibly through the formation of hydrogen bonds. Hydrogen fluoride is associated in the vapor state, and in solution is thought to give rise to $[HF_2]^-$ ions. This is evidence favoring the formation of hydrogen bonds.

The writer has undertaken a series of experiments on mixtures of liquids in which association of the two liquids may be anticipated through the formation of hydrogen bonds. Liquids, such as water, alcohols, aniline, were mixed with acetone, ethers, methyl cyanide, ethyl formate, ethyl acetate, etc. Changes in the electric moment of the group which carry the hydrogen would be expected if hydrogen bonds are formed. These variations would be evidenced by changes in the infrared spectra. Preliminary results show that changes in the spectrum actually exist, which may be attributed to this. For example, in mixtures of methyl alcohol and ethyl acetate, the fundamental vibrational band of the OH alcohol group is shifted to the shorter wave-length and its intensity is appreciably increased, while the vibrational band of the CO group in the ethyl acetate is shifted to the longer wave-length with a corresponding increase in intensity. Other bands appear to remain constant. Similar results were obtained for other alcohol mixtures and for aniline with several other organic liquids. Also changes in the water spectrum indicate association between water and methyl cyanide, and water and other organic liquids.

It is expected that these results will be ready for publication soon.

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October 12, 1936.

[1] L. Pauling, J. Am. Chem. Soc. **57**, 2680 (1935); ibid. **58**, 94 (1936); L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936); R. H. Gillette and A. Sherman, J. Am. Chem. Soc. **58**, 1135 (1936); R. H. Gillette and F. Daniels, J. Am. Chem. Soc. **58**, 1139 (1936).